Soft and Hairy

A bio-inspired approach to lubricate engineering materials with water

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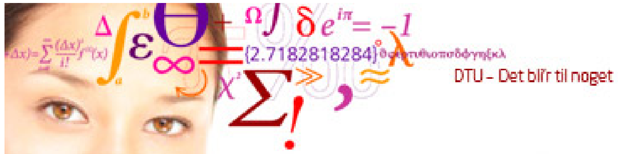

Soft and Hairy:
A Bio-inspired Approach to Lubricate Engineering Materials with Water

Plast, friktion og non-stick

Torsdag 15. april, kl. 9.00 – 16.00

i Ingeniørhuset, Kalvebod Brygge 31 – 33, København V

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Water as a lubricant

Oil

Men's primary choice of lubricant

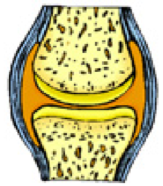
Challenges in oil-based lubrication:

limited resources

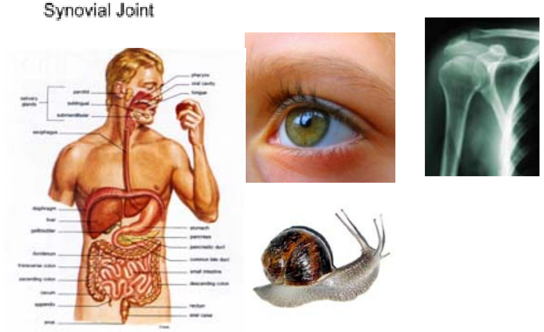
environmental issue (especially additives)

Water

Nature's primary choice of lubricant



Synovial Joint



μ for human cartilage: as low as 0.001!

Water as a lubricant: Engineers' point of view

- non-toxic
- environmentally-friendly
- readily available and cost effective
- non-flammable
- high thermal capacity
- biocompatible

- **poor pressure response**

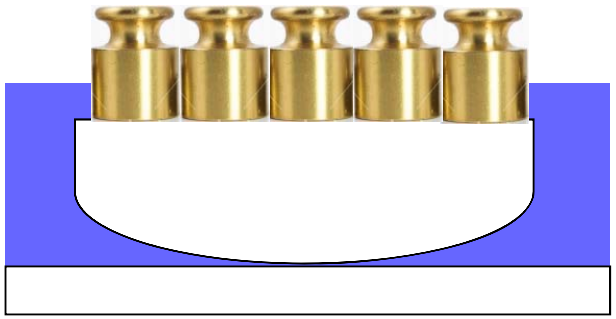
low pressure-coefficient of viscosity

water: $\alpha = 0.36\ GPa^{-1}$

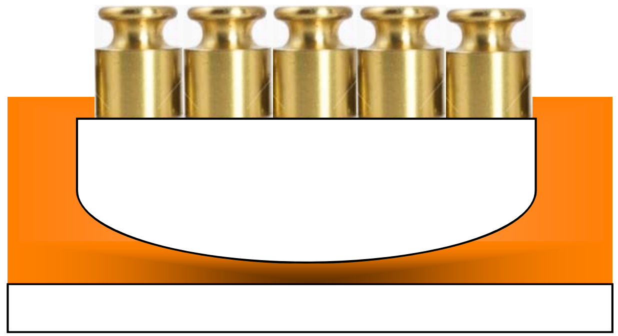
oil: $\alpha = 10\text{-}20\ GPa^{-1}$

- limited application temperature
- corrosion for ferrous materials

water

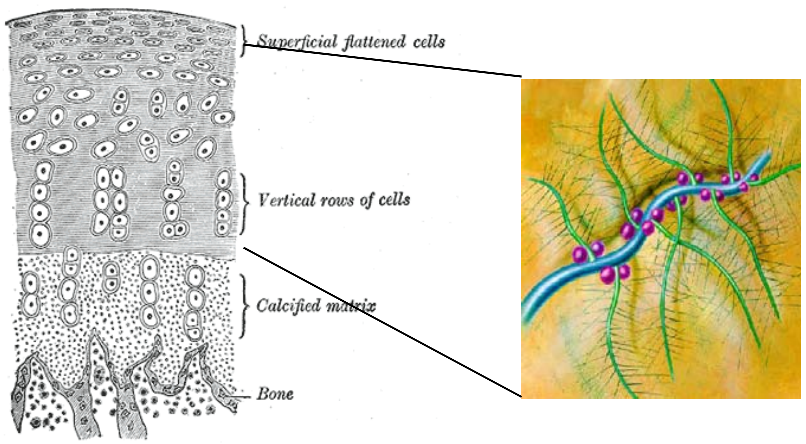


oil



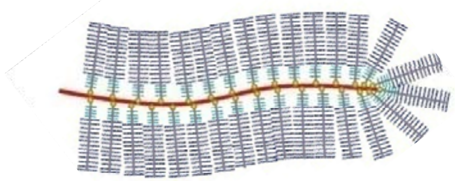
Nature’s approach to use water as lubricant – recipe 1

brush-like, ***sugar-based*** macromolecules – **Keep the surface hydrophilic !**



Proteoglycan aggregate

- plays a key *structural role* in cartilage



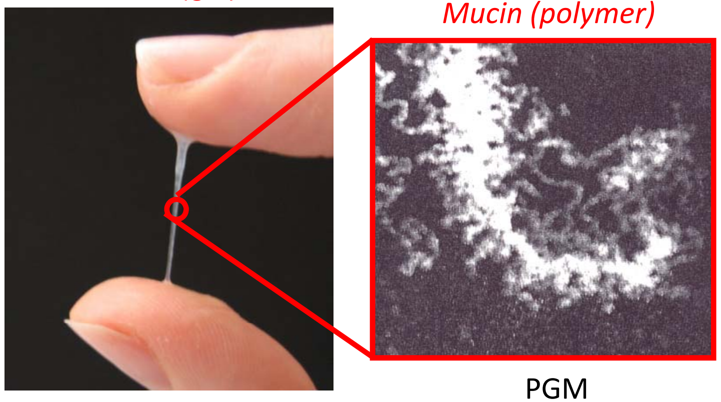
sugar chains
link protein
core protein
hyaluronan

S. Lee et al., **SCIENCE** 2008

Mucins

Mucus (gel)

Mucin (polymer)

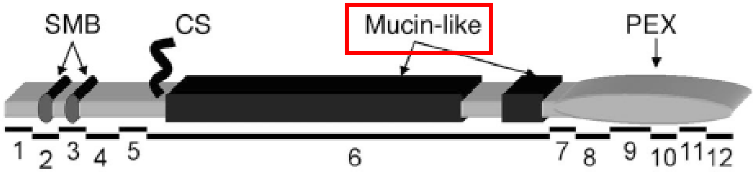


PGM
(STM, 360 nm × 360 nm)

Roberts, CJ et al Proteins and Peptide Letters 1995 2, 409

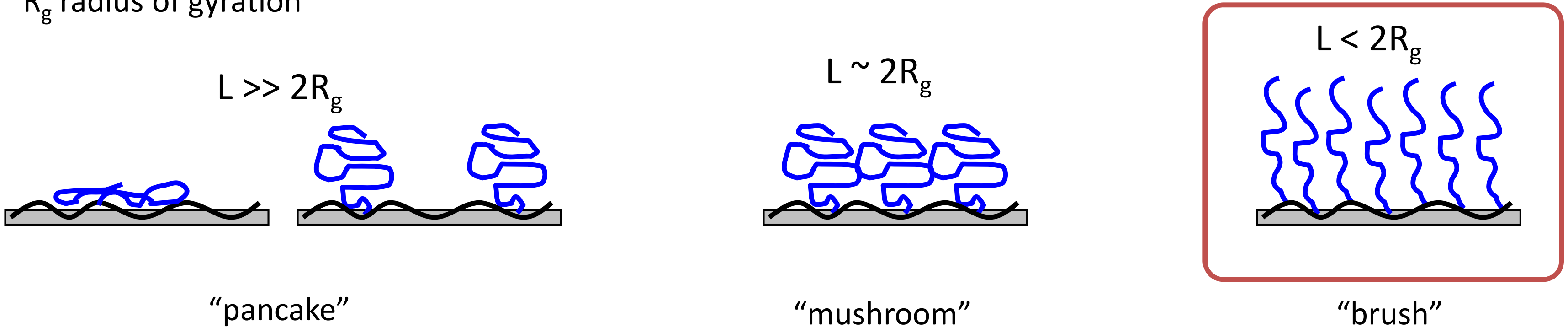
Lubricin

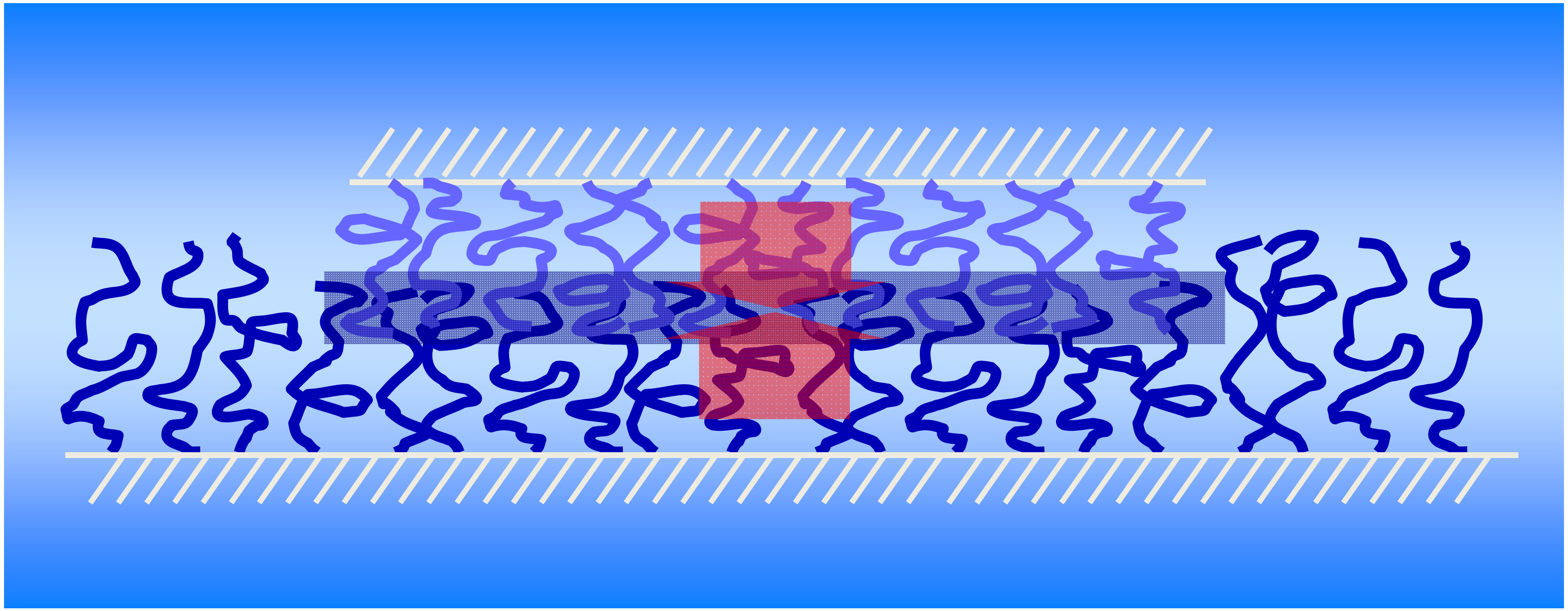
- mucinous glycoprotein of the synovial fluid (250 μg/ml, MW = 2.3×10^5 g/mol)



End-tethered, “brush-like” polymer chains

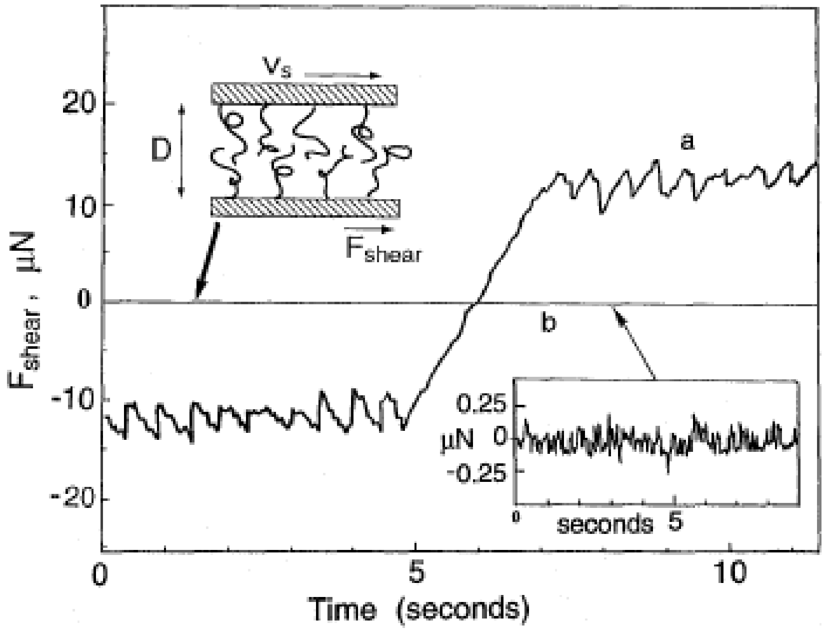
L distance between grafted chains
R_g radius of gyration





End-tethered, “brush-like” polymer chains

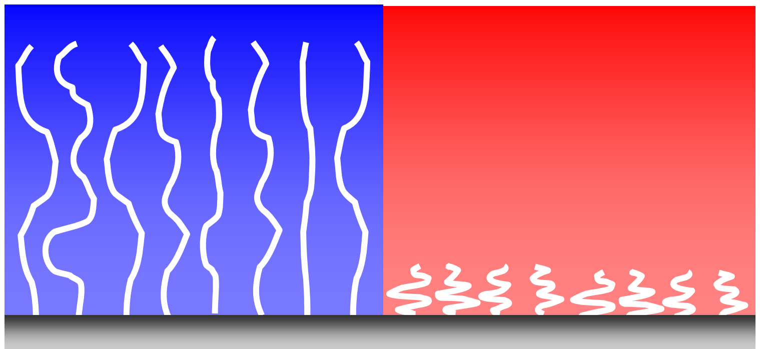
Polystyrene/toluene



J. Klein Ann. Rev. Mat. Sci. 1996, 260, 581-612

“good” solvent

“poor” solvent



Poly(ethylene glycol) (PEG)

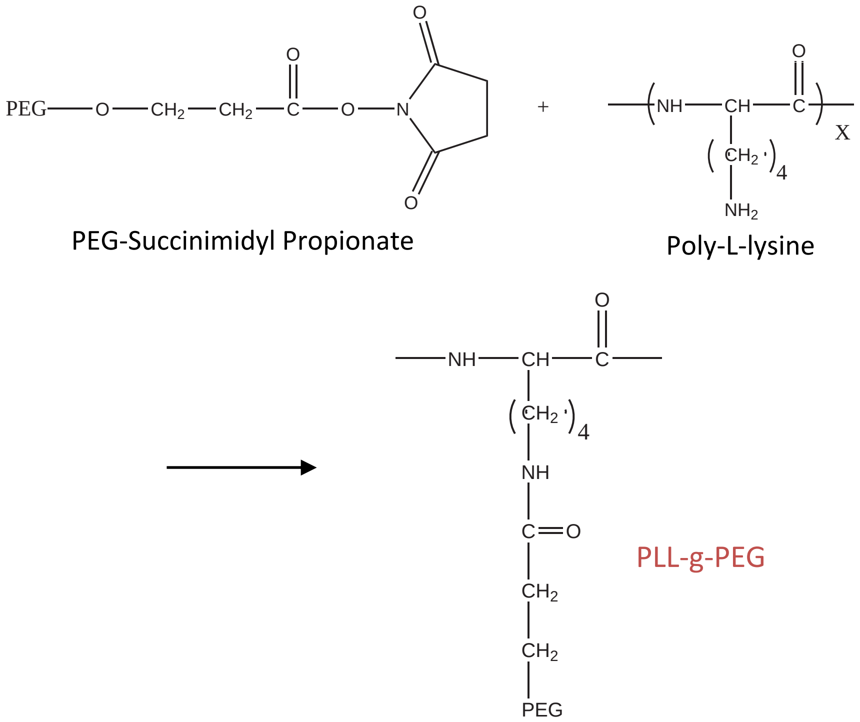
Poly(ethylene oxide) (PEO)

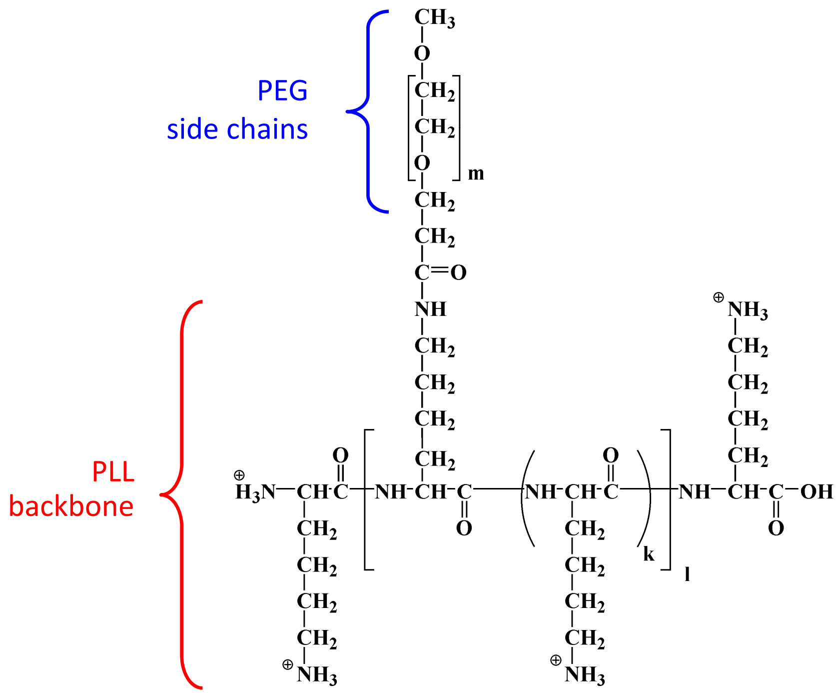
PEG and PLL-*g*-PEG

Poly(ethylene glycol) (PEG)

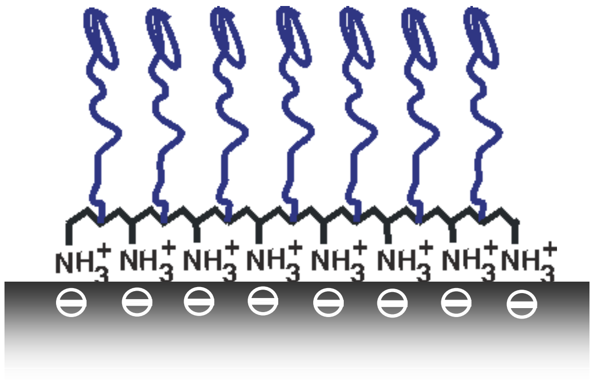
- water-soluble
- pharmaceutical applications, surfactants, colloidal stabilization
- anti biofouling properties: biosensor applications

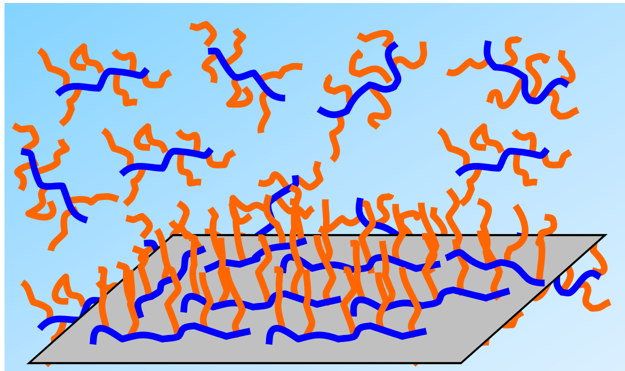
Poly(L-lysine)-graft-poly(ethylene glycol) (PLL-*g*-PEG)



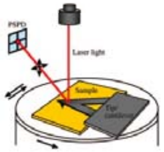


Adsorption of PLL-*g*-PEG onto negatively charged surfaces

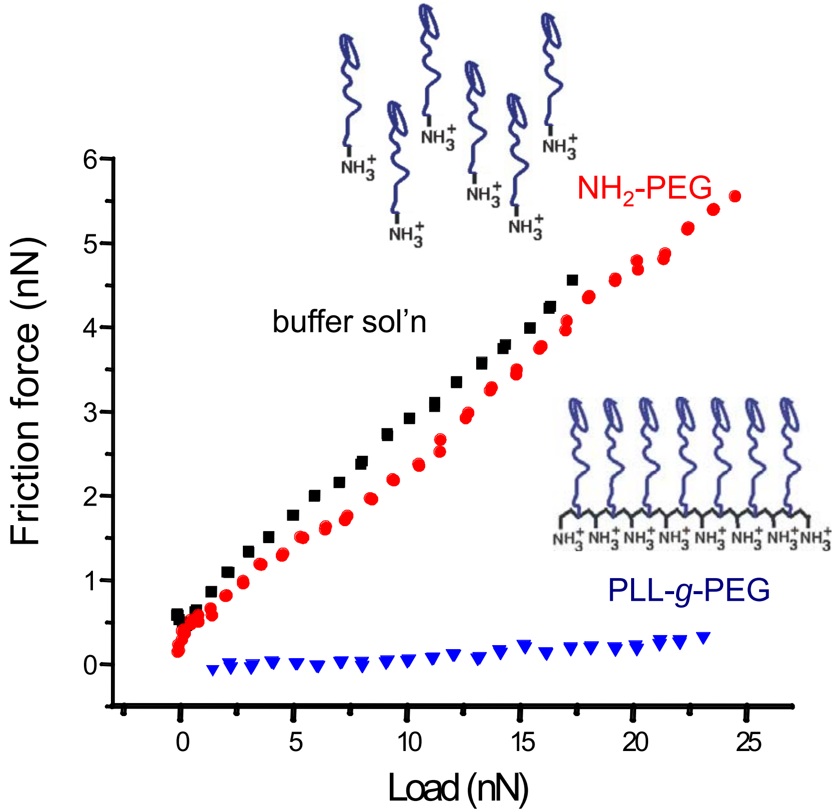


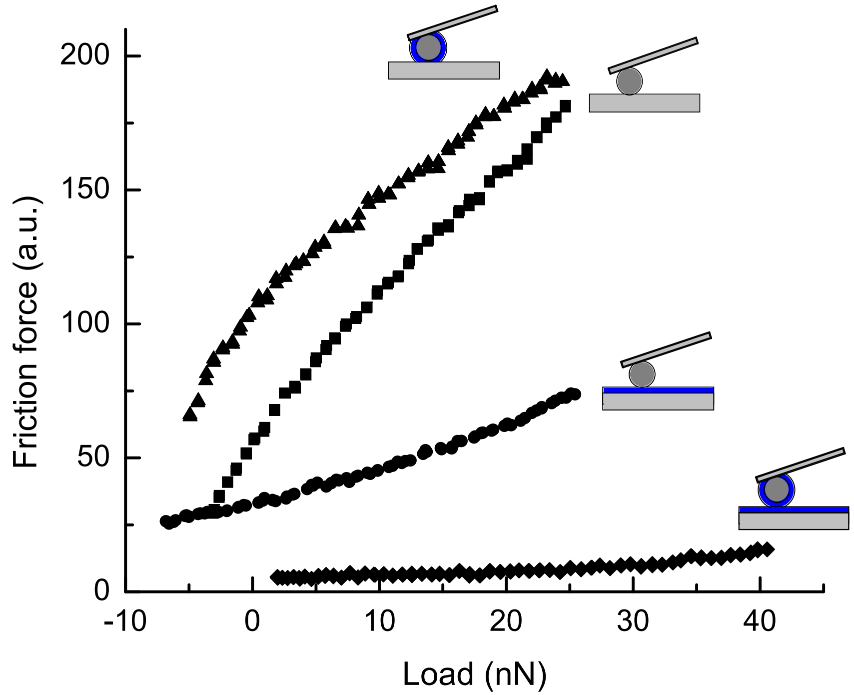


Nanotribological properties of PLL-*g*-PEG



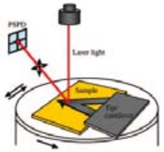
SiO$_2$/SiO$_2$ contact in aq. buffer (pH 7)





X. Yang et al., **Langmuir** 2004, 20, 423

Influence of structural features: PEG chain length

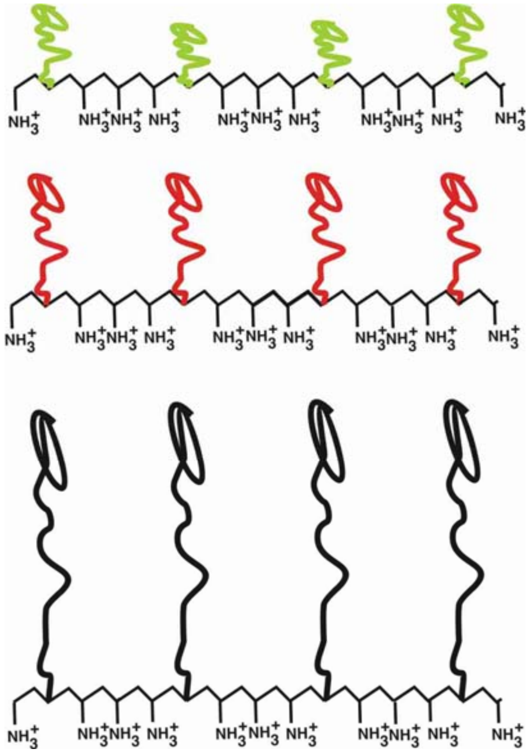


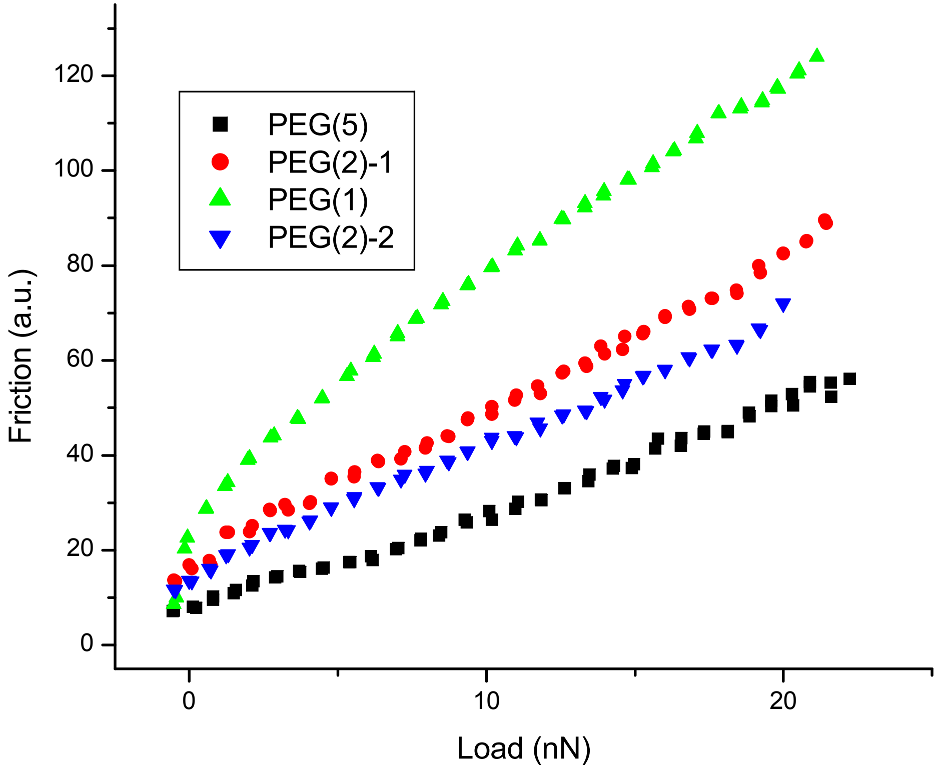
SiO$_2$/SiO$_2$ contact in aq. buffer (pH 7)

1 kDa

2 kDa

5 kDa

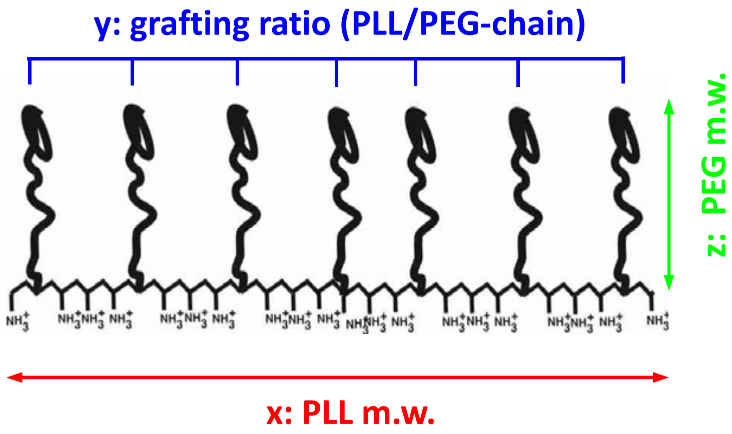




X. Yang et al., **Langmuir** 2004, 20, 423

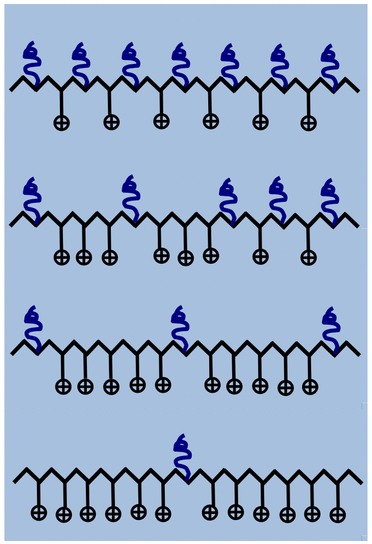
Influence of structural features: PEG length & Grafting ratio

Architectural parameters: PLL(x)-g[y]-PEG(z)

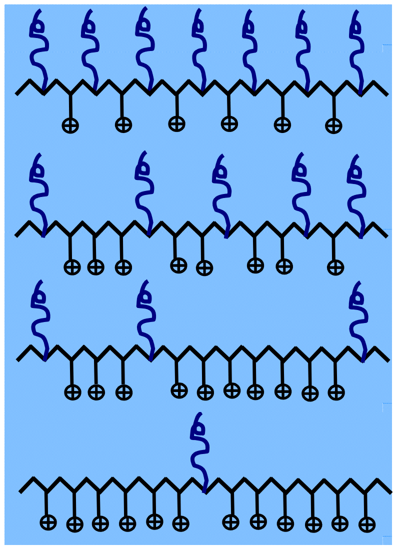


PLL Mw. [kDa]	grafting ratio *g* (Lys/PEG ratio)	PEG Mw. [kDa]
20	3.4	2
20	5.7	2
20	8	2
20	14.2	2
20	3.5	5
20	5.2	5
20	8	5
20	11.4	5
20	5.8	10
20	7.6	10
20	15.7	10

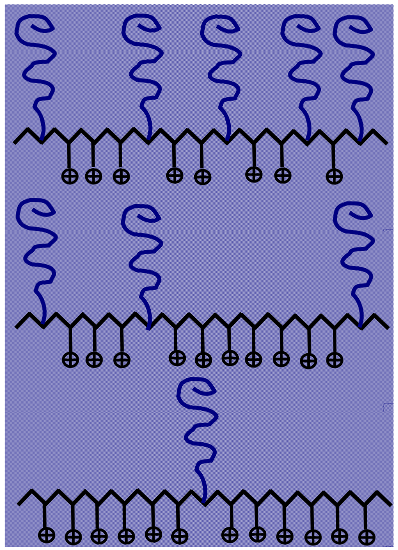
PEG 2kDa



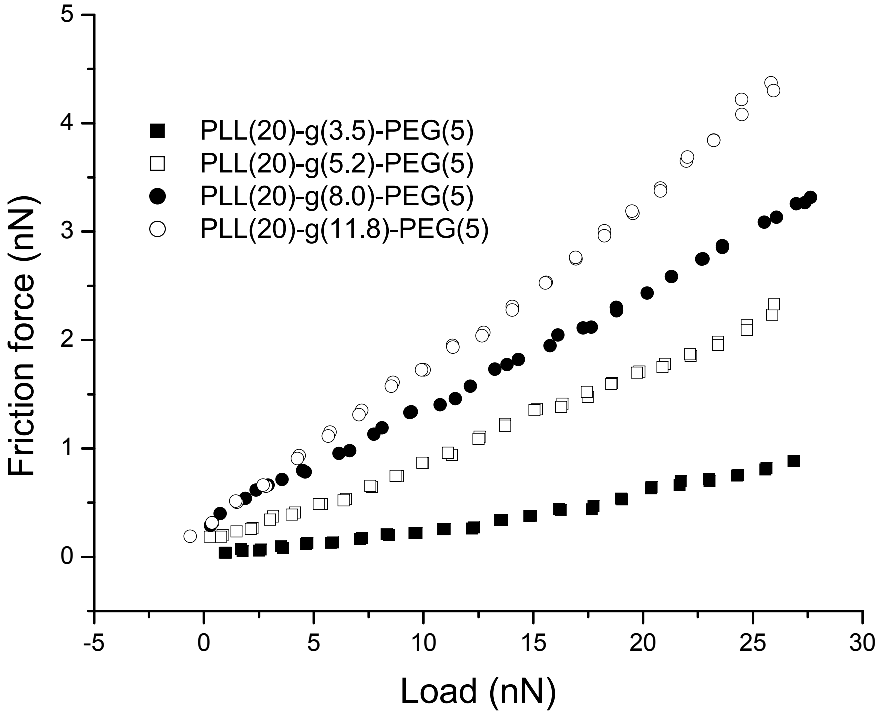
PEG 5kDa



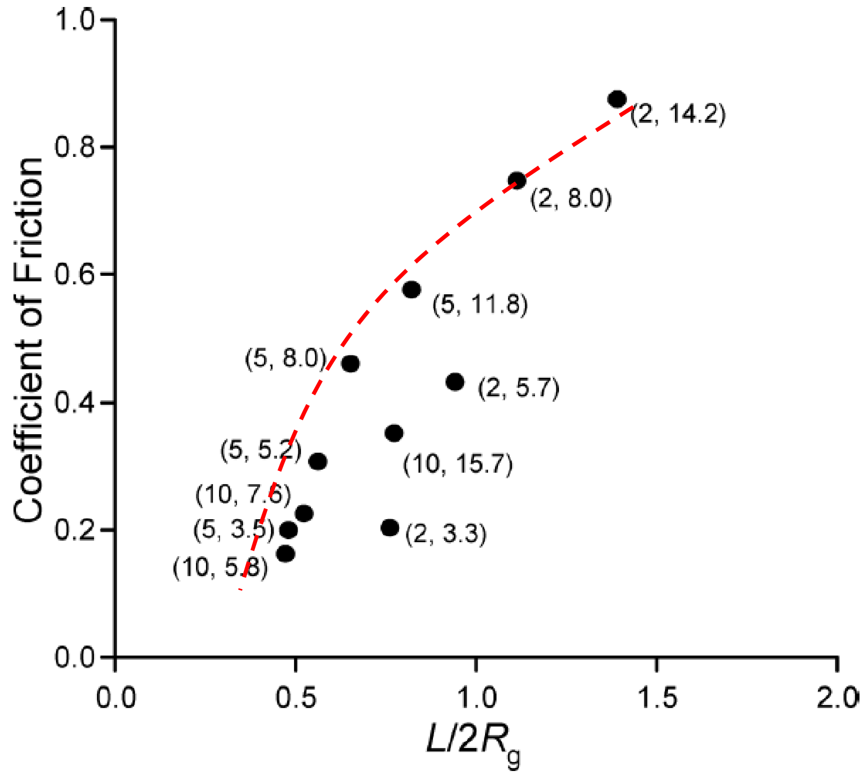
PEG 10 kDa



Nanotribological properties of PLL-*g*-PEG



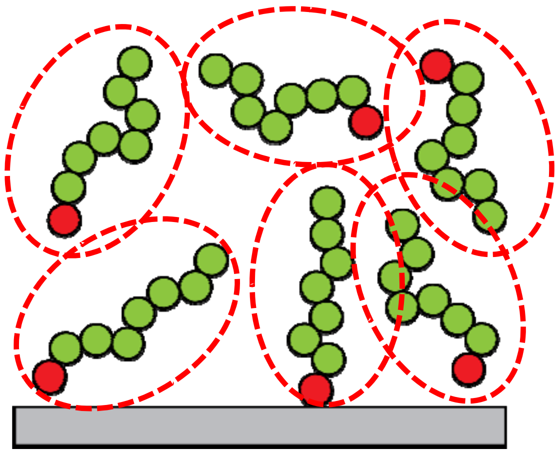
(m.w., grafting ratio)



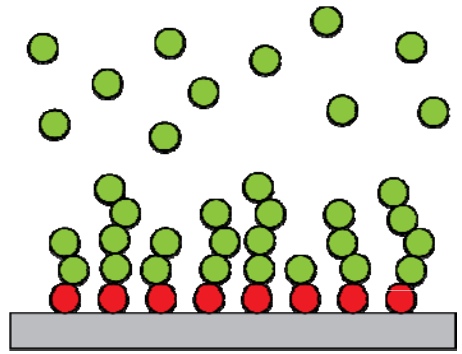
S.S. Perry et al., **Applied Materials & Interfaces**2009, 1, 1224

Grafting-to vs. Grafting-from approaches

grafting-to



grafting-from



Experimentally straightforward

Steric/electrostatic repulsion

Limited surface adsorption

High surface grafting density

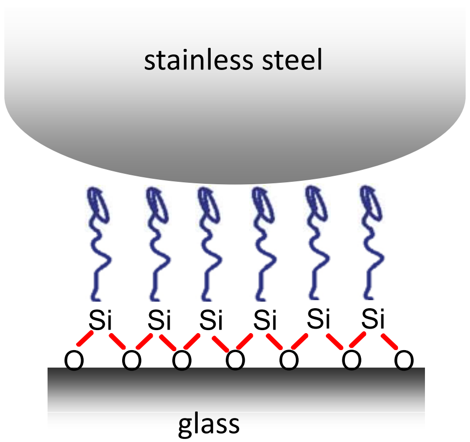
High molecular weights

Experimentally more demanding

Variety of brush architectures

Design of polymer lubricant additives

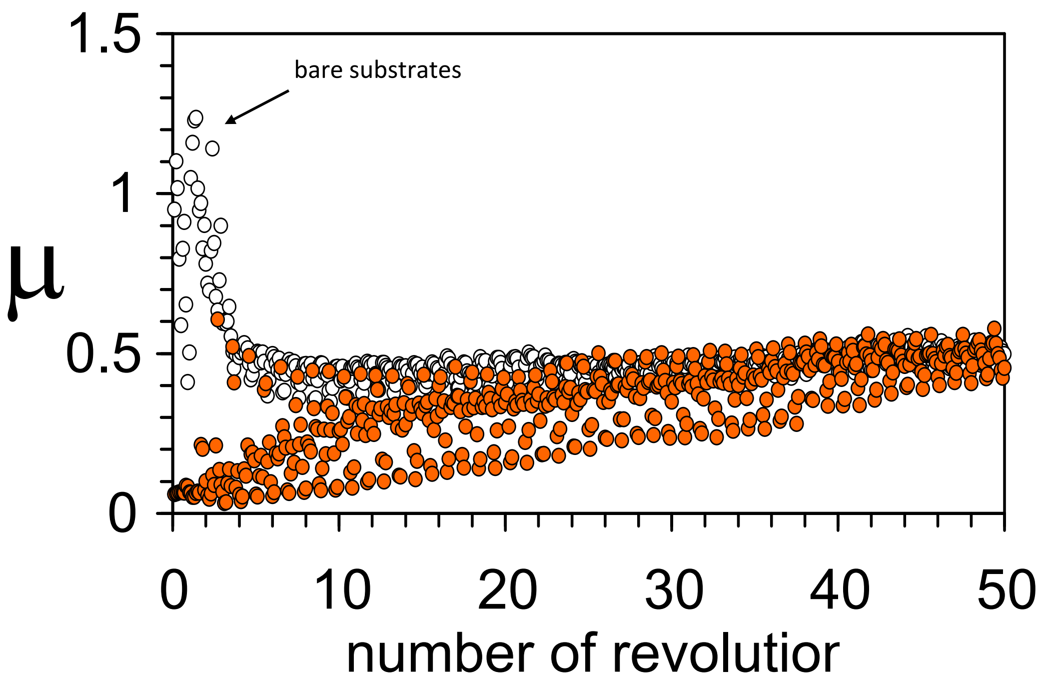
Polymers with ***strong*** bonding onto surface



Silane-PEG

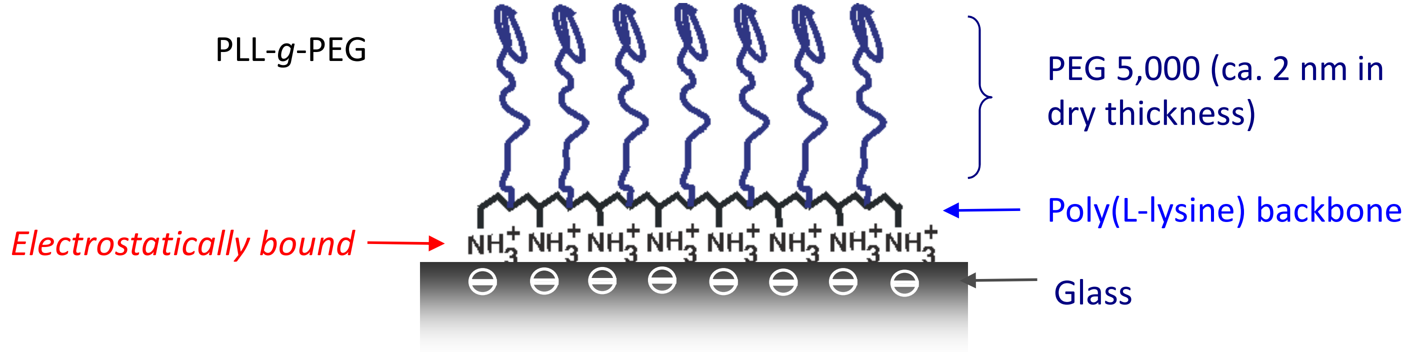
Pin-on-disk tribometry

2 N, ca. 5.1 GPa

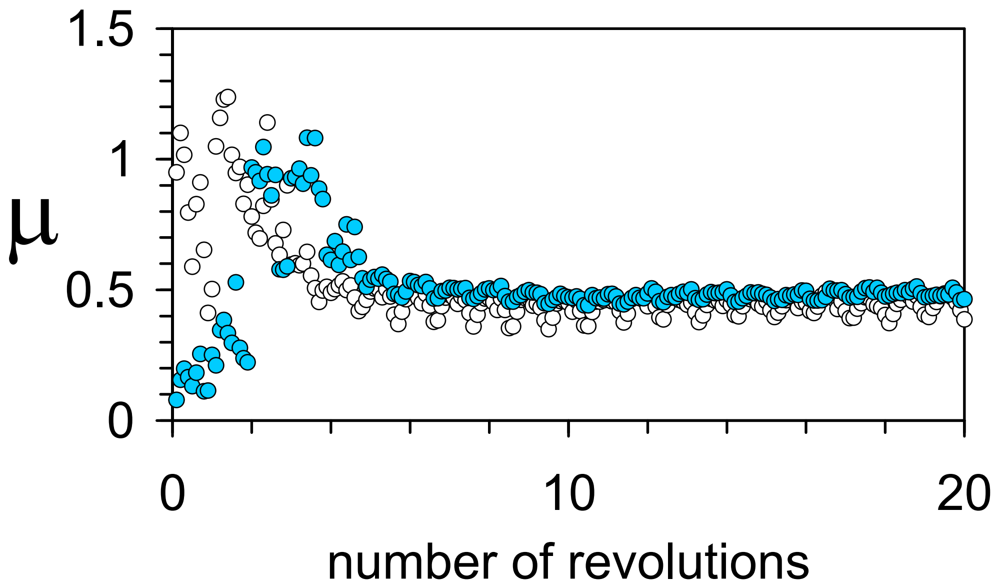


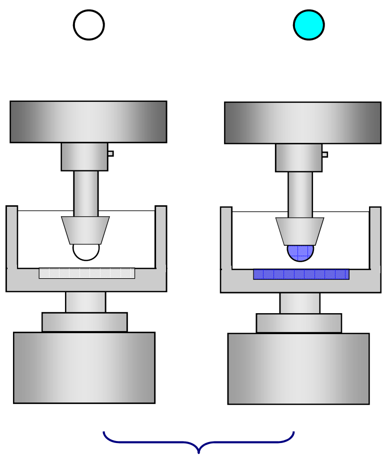
“Self-healing”

Polymers with ***fast*** surface-adsorption kinetics



Against stainless steel pin (2 N, ca. 5.1 GPa)

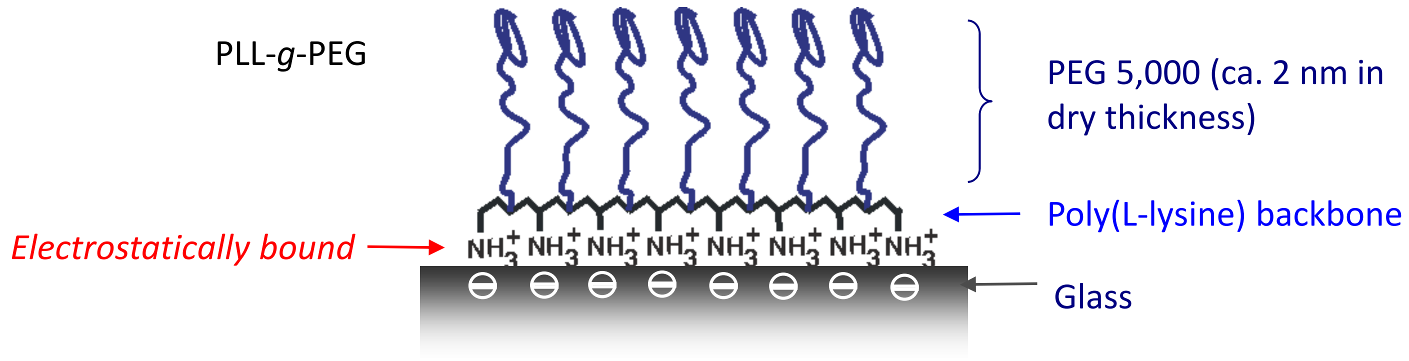




S. Lee et al., **Tribol. Lett.** 2005, 24, 217

“Self-healing”

Polymers with ***fast*** surface-adsorption kinetics



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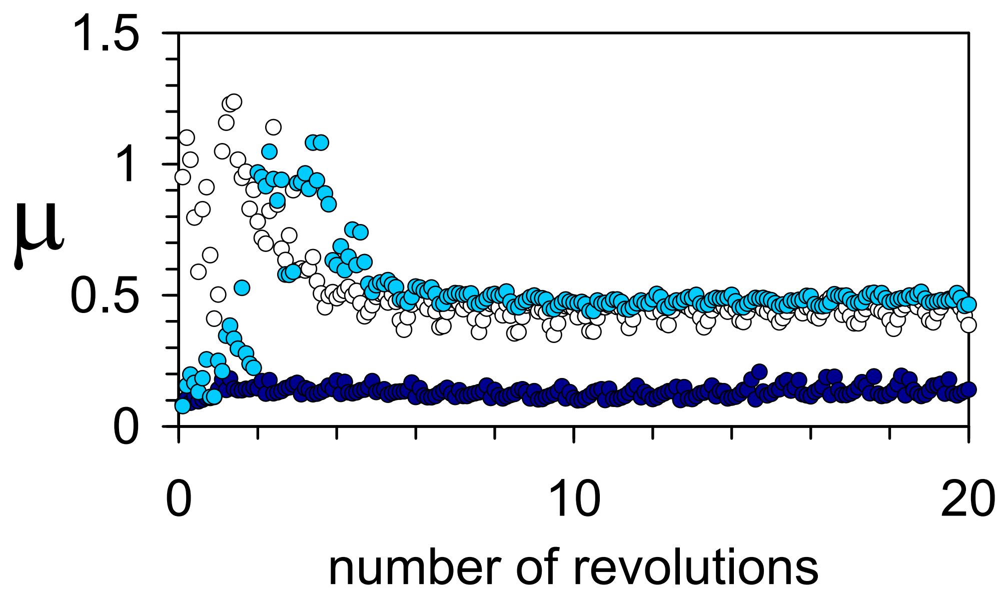
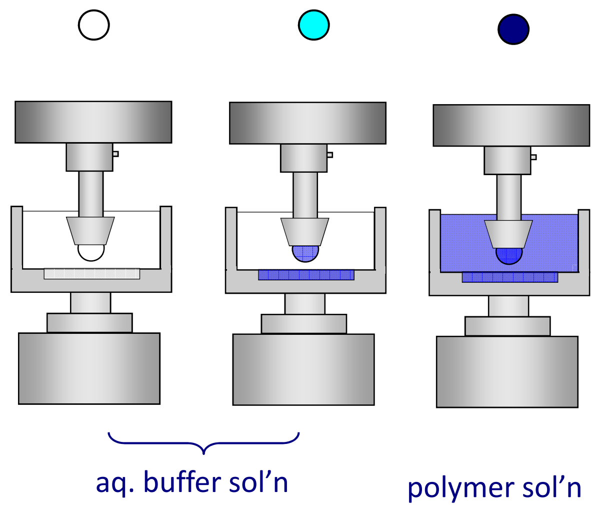
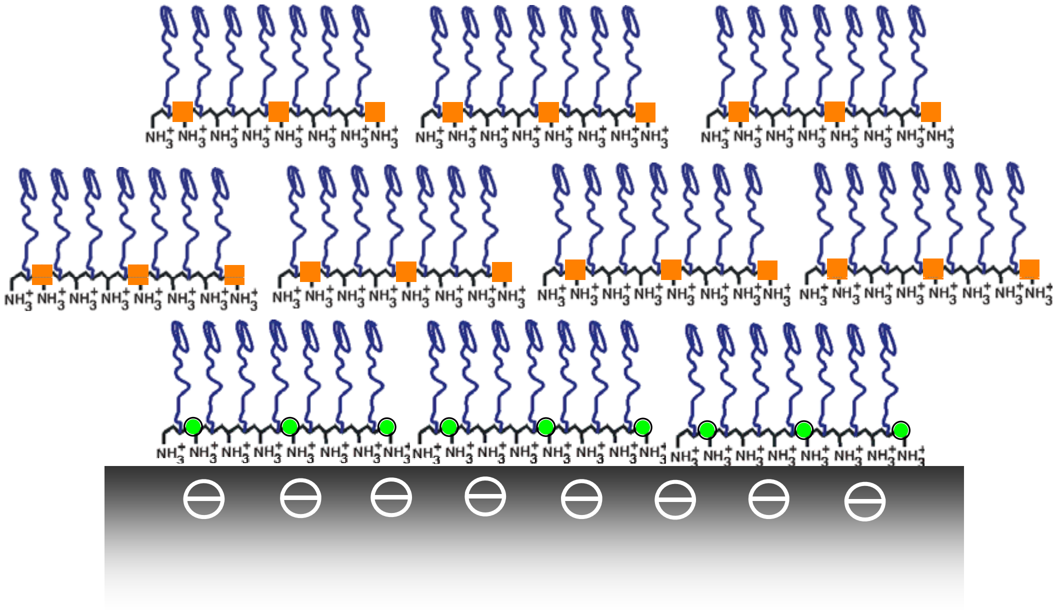


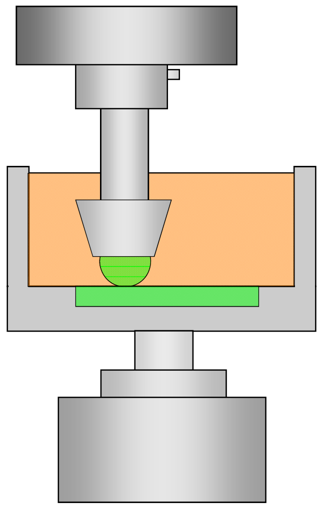


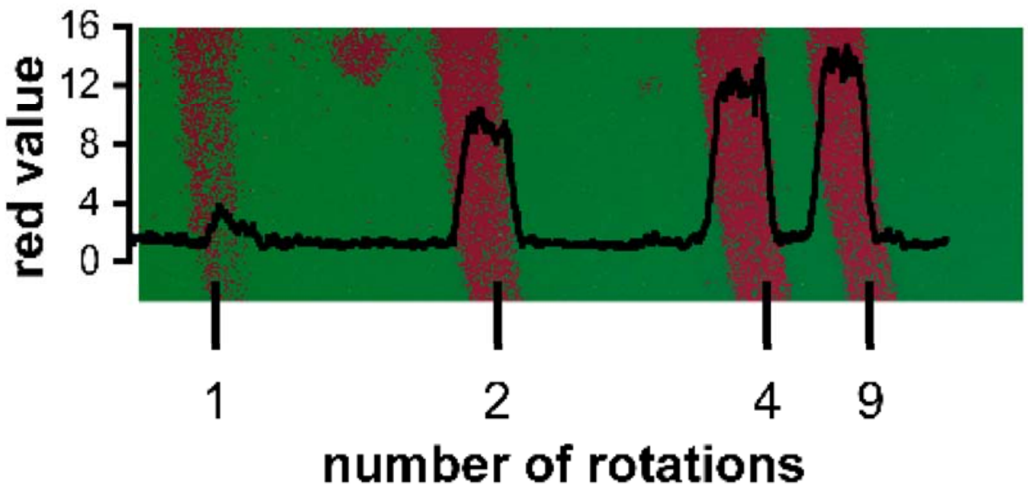
S. Lee et al., **Tribol. Lett.** 2005, 24, 217

“Self-healing”

Fluorescence-labeling







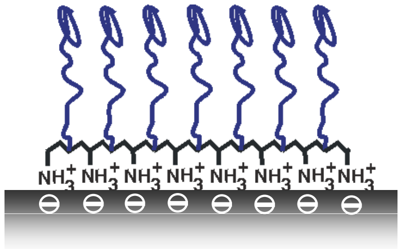
S. Lee et al., **Tribol. Lett.** 2005, 24, 217

Lubrication of hard surfaces with water: challenging oils

Assisted by brush-like polymer chains

Steel vs. Glass

PLL-*g*-PEG



negatively charged surfaces

Steel: most popular materials for bearings and gears

Glass: negatively charged surfaces in neutral aq. solution

optical reflectance and transparency (requirements in measurement principle)

Pin-on-disk tribometry

friction (sliding contact)

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.

Mini-Traction Machine (MTM)

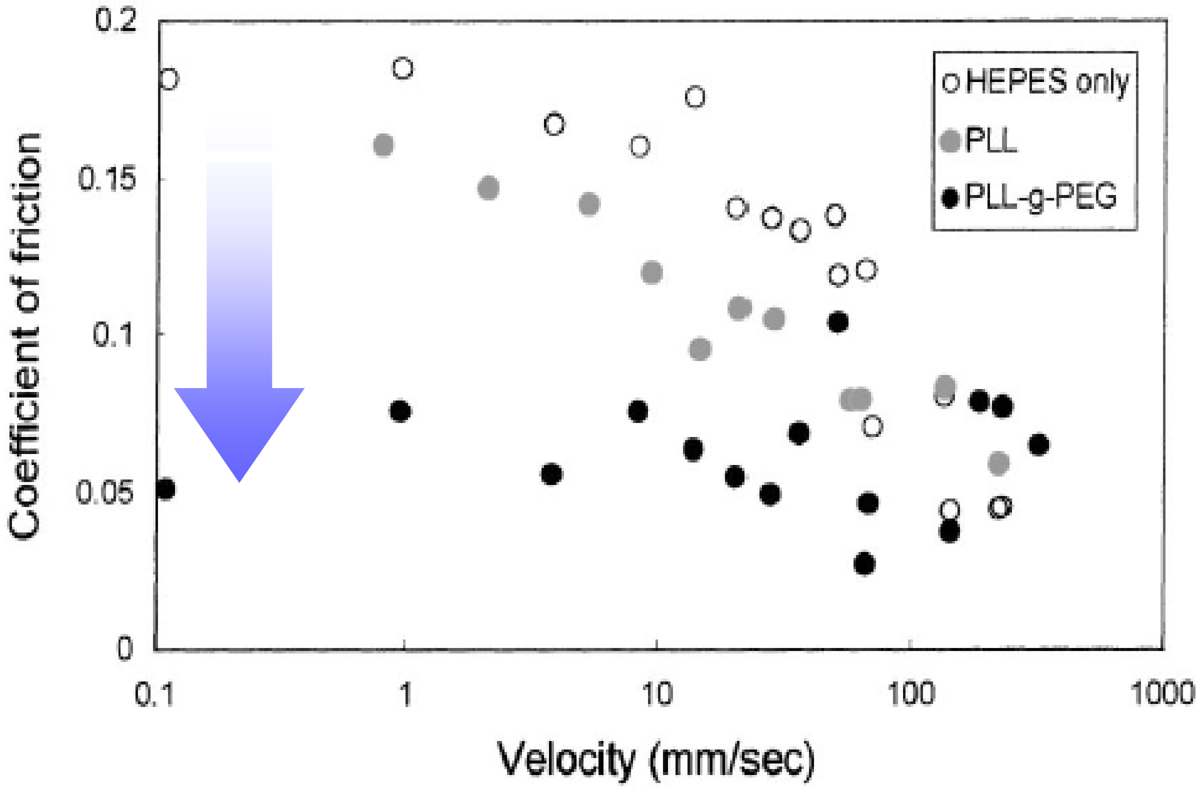
friction (sliding/rolling contact)

EHL rig

film thickness (sliding/rolling contact)

Boundary lubrication: Low-speed regime

Pin-on-disk tribometry

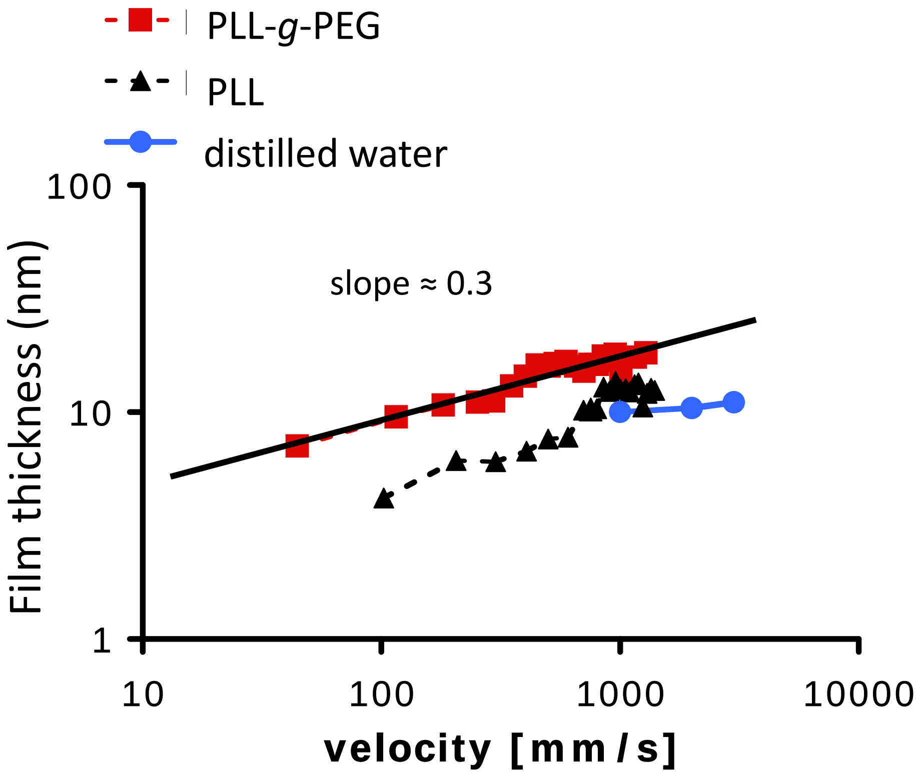


S. Lee et al., **Tribol. Lett**. 2003, 15, 231

Transition to EHL regime ?

fluid-film lubrication in high-speed regime

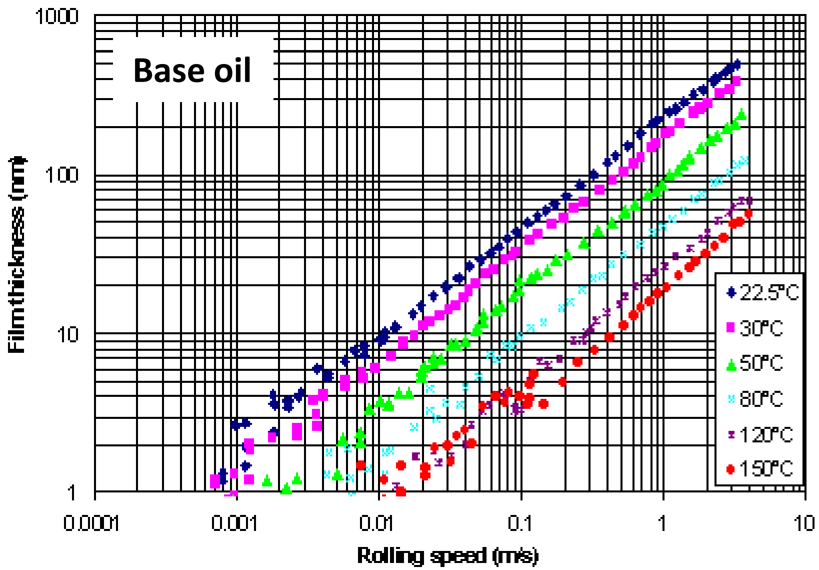
Under 20 N



Elastohydrodynamic Lubrication

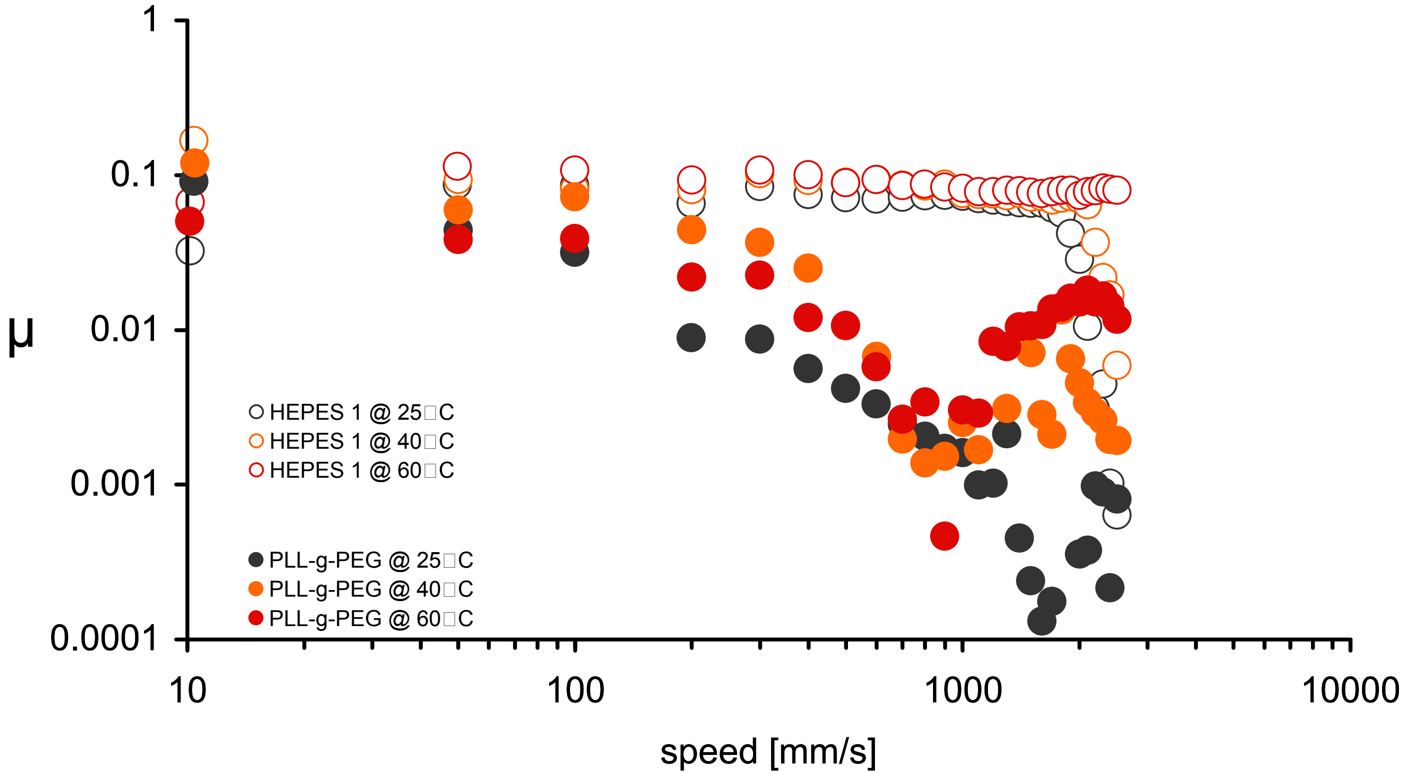
$$h \propto (U \cdot \eta)^{0.67} \cdot (\alpha)^{0.5}$$

h: film thickness
U: mean speed
η: viscosity
α: pressure-viscosity coefficient



M. Müller et al., **Tribol. Lett.** 2003, 15, 395

Temperature effect



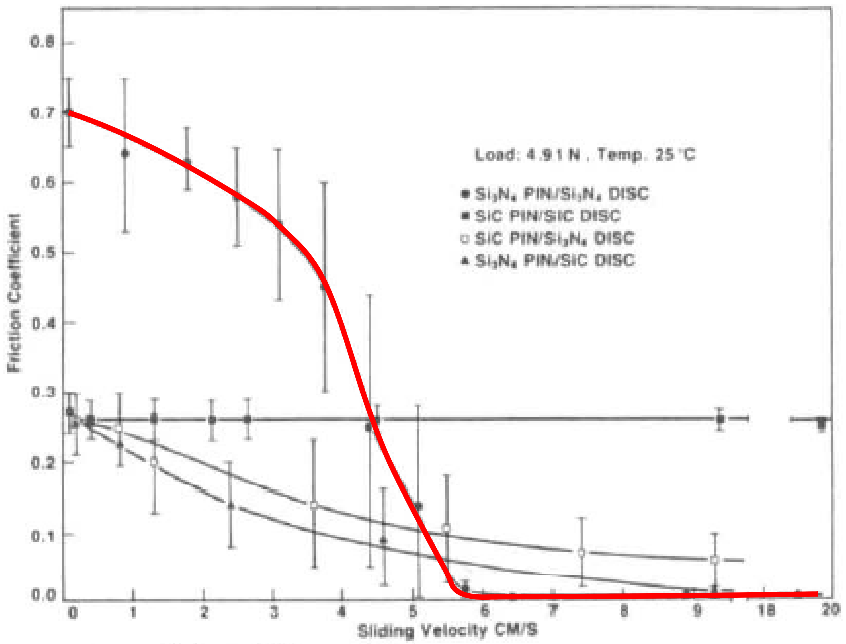
Non-ferrous bearing materials: Ceramics

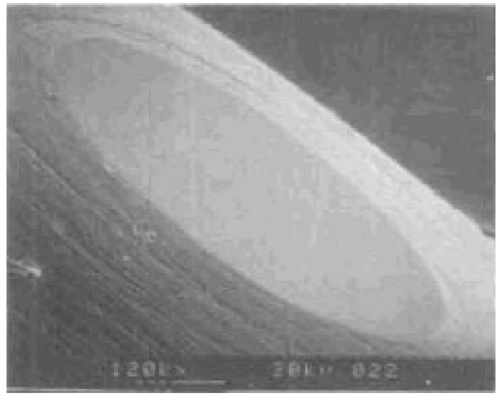
ZrO_2, Si_3N_4, SiC, Al_2O_3 etc.

compared to steel ....

non-conductive
higher wear resistance
higher thermal stability
corrosion-free by water

Extremely low friction forces by Si_3N_4



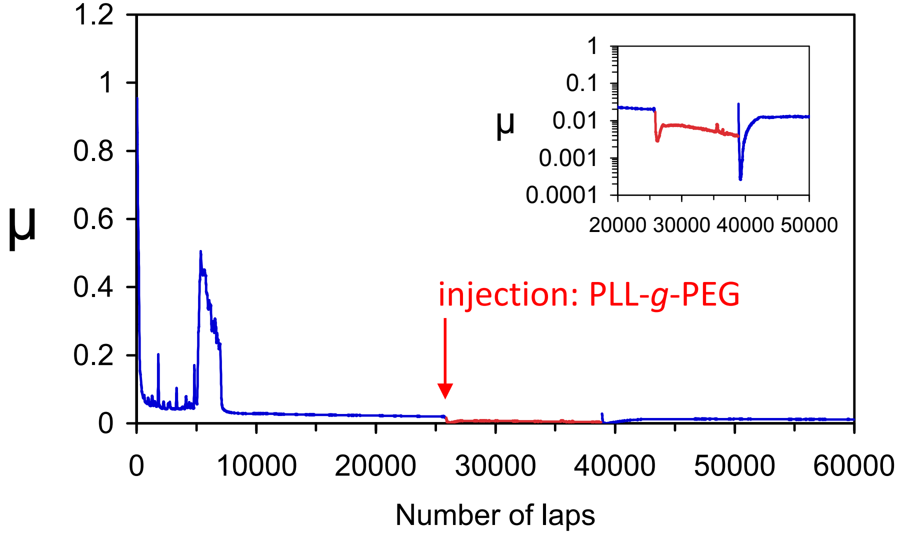


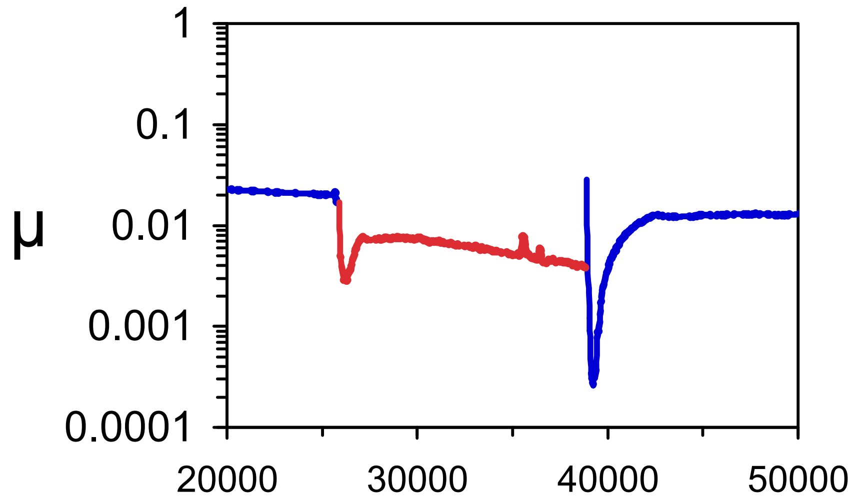
$$Si_3N_4 + 6H_2O \rightarrow 3SiO_2 + 4\ NH_3$$

H. Tomizawa et al., **Tribol. Trans.** 1987, 30, 41

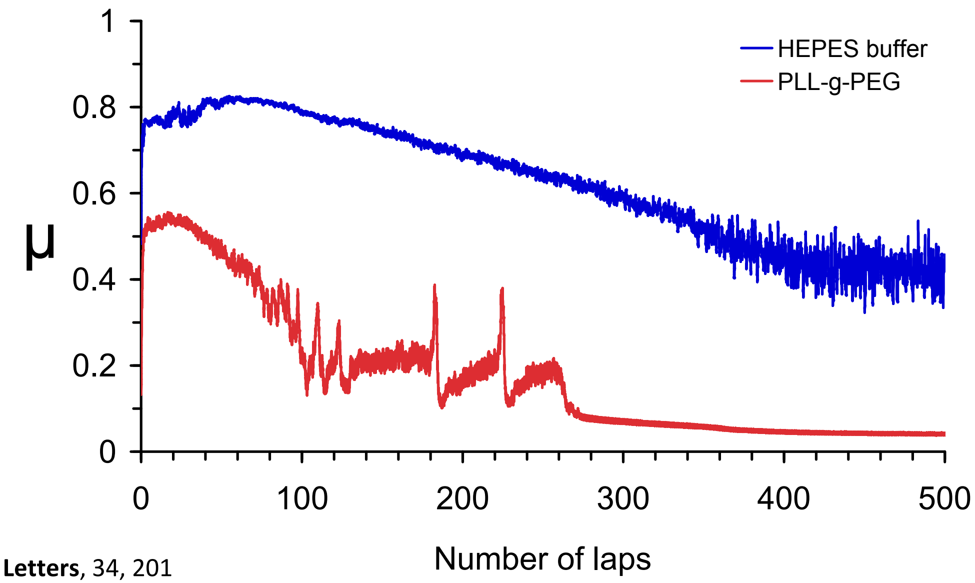
Lubrication of Si_3N_4 by brush-like polymers

Under **120** mm/s, 5 N





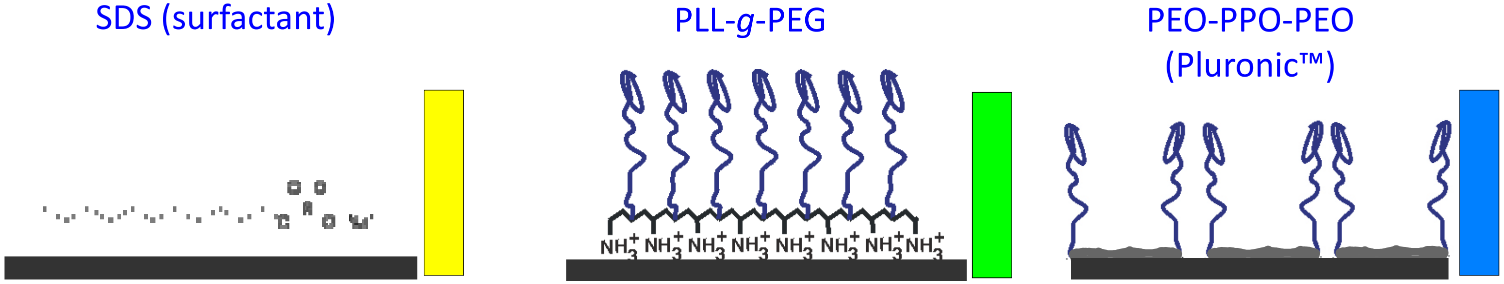
Under **10** mm/s, 5 N



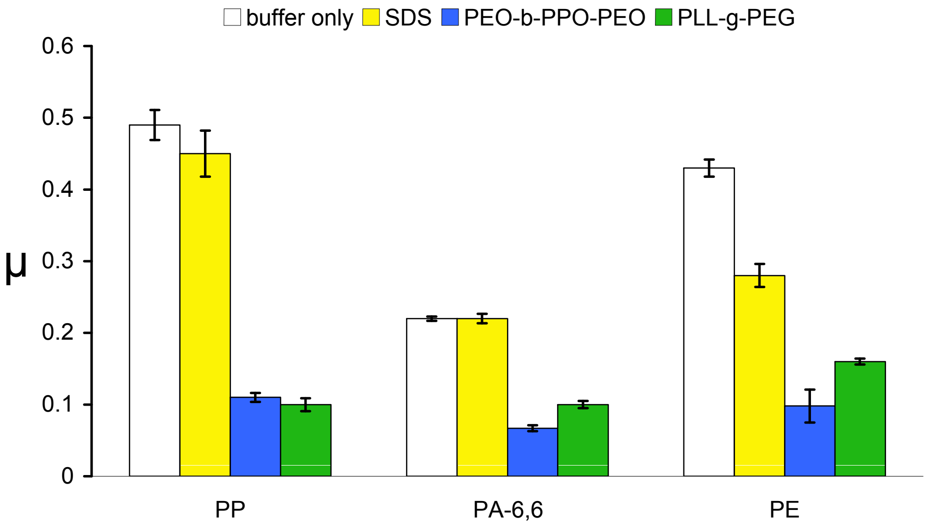
W. Hartung et al., **Tribology Letters**, 34, 201

Non-ferrous bearing materials: Thermoplastics

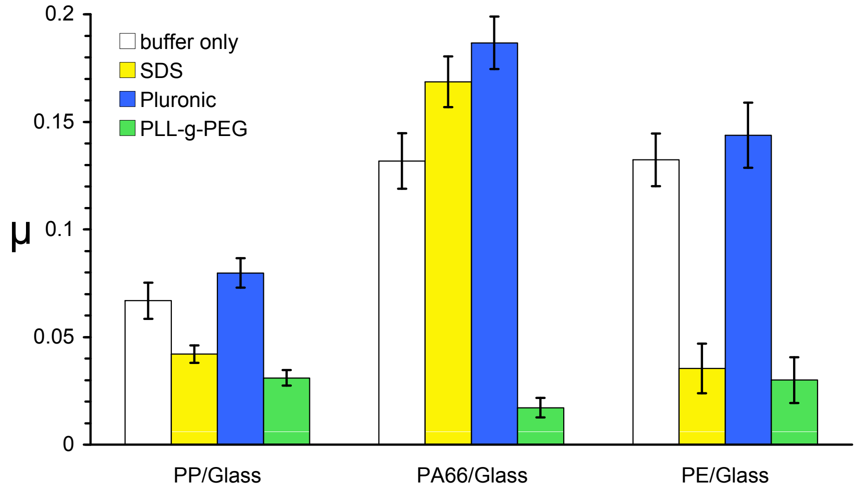
PE, PP, PVC, PTFE, PA 6,6, EVA etc.



self-mating



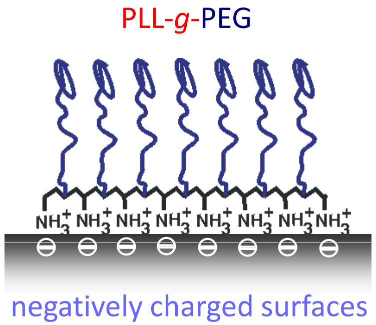
against steel

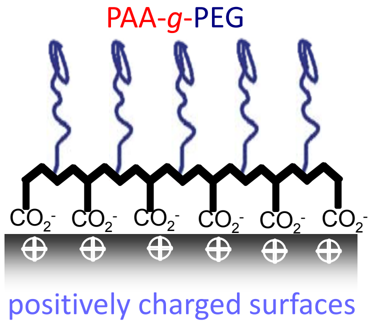


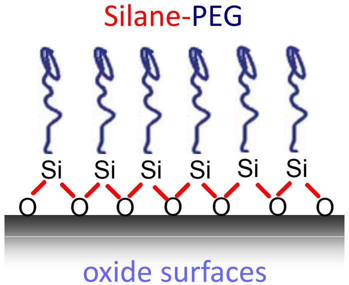
S. Lee et al., **Lub. Sci.** 2008, 20, 21

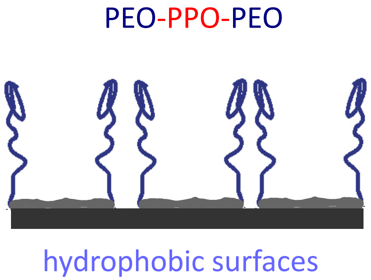
Alternative copolymers

Anchor

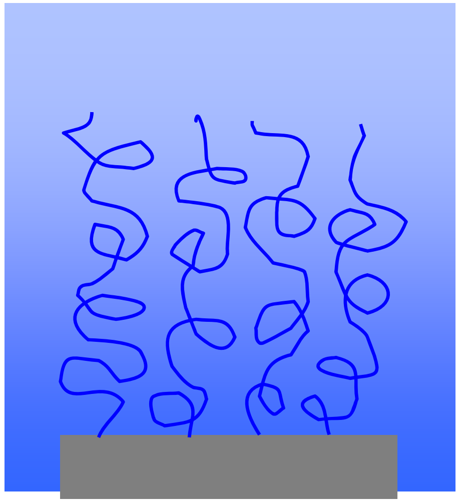








Brush



poly(ethylene glycol) (PEG)

acrylic amide (AAm)

N,N-dimethyl acrylamide (DMAAm)

poly(N-vinyl-2-pyrrolidone) (PNVP)

poly(2-hydroxyethyl metharcrylate) (PHEMA)

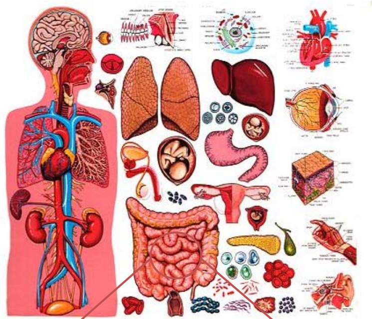
poly(vinyl alcohol) (PVA)

poly(metharcrylate)-PEG

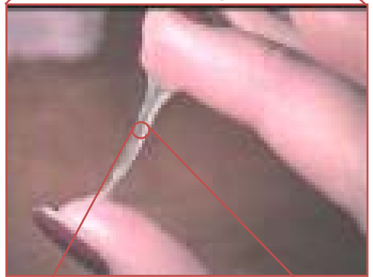
poly(acrylic acid) (PAA)

- Biomaterials 1994, Y. Ikada

Biological lubricant additives are “sweet”



mucus (gel)



Water

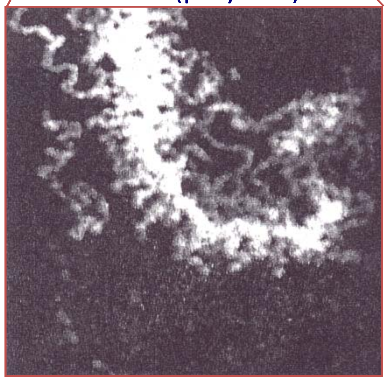
Salts

IgG

Proteins

mucins

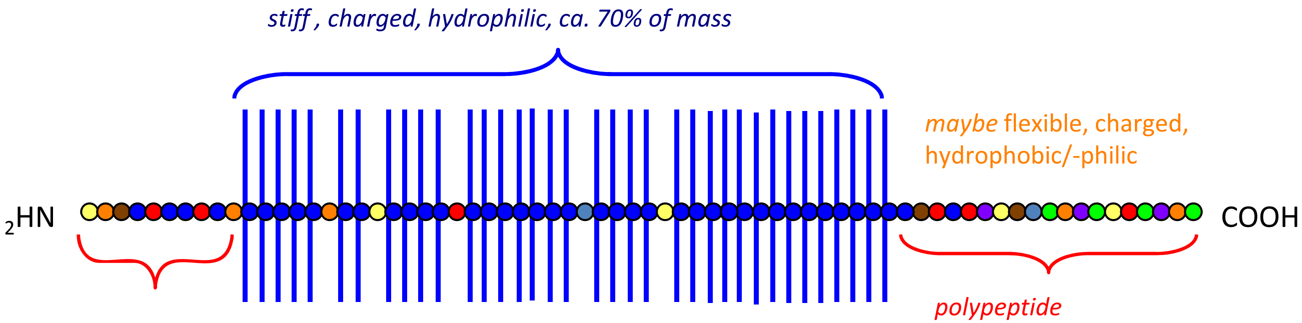
mucin (polymer)



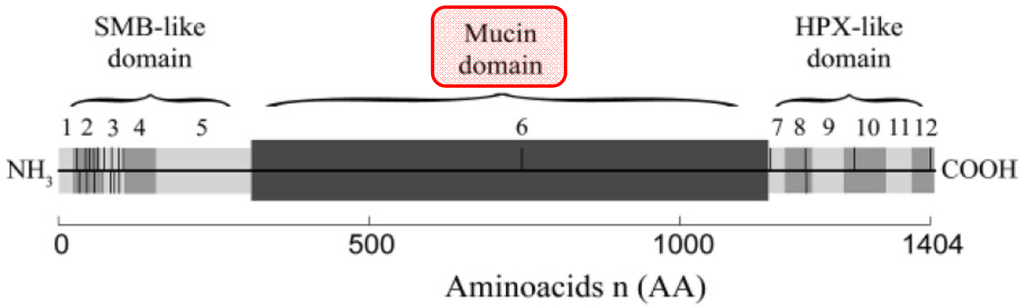
PGM, STM (360 nm × 360 nm)

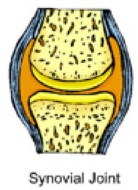
Roberts, CJ et al, **Proteins and Peptide Letters** 1995, 2, 409

Schematic representation of the mucin



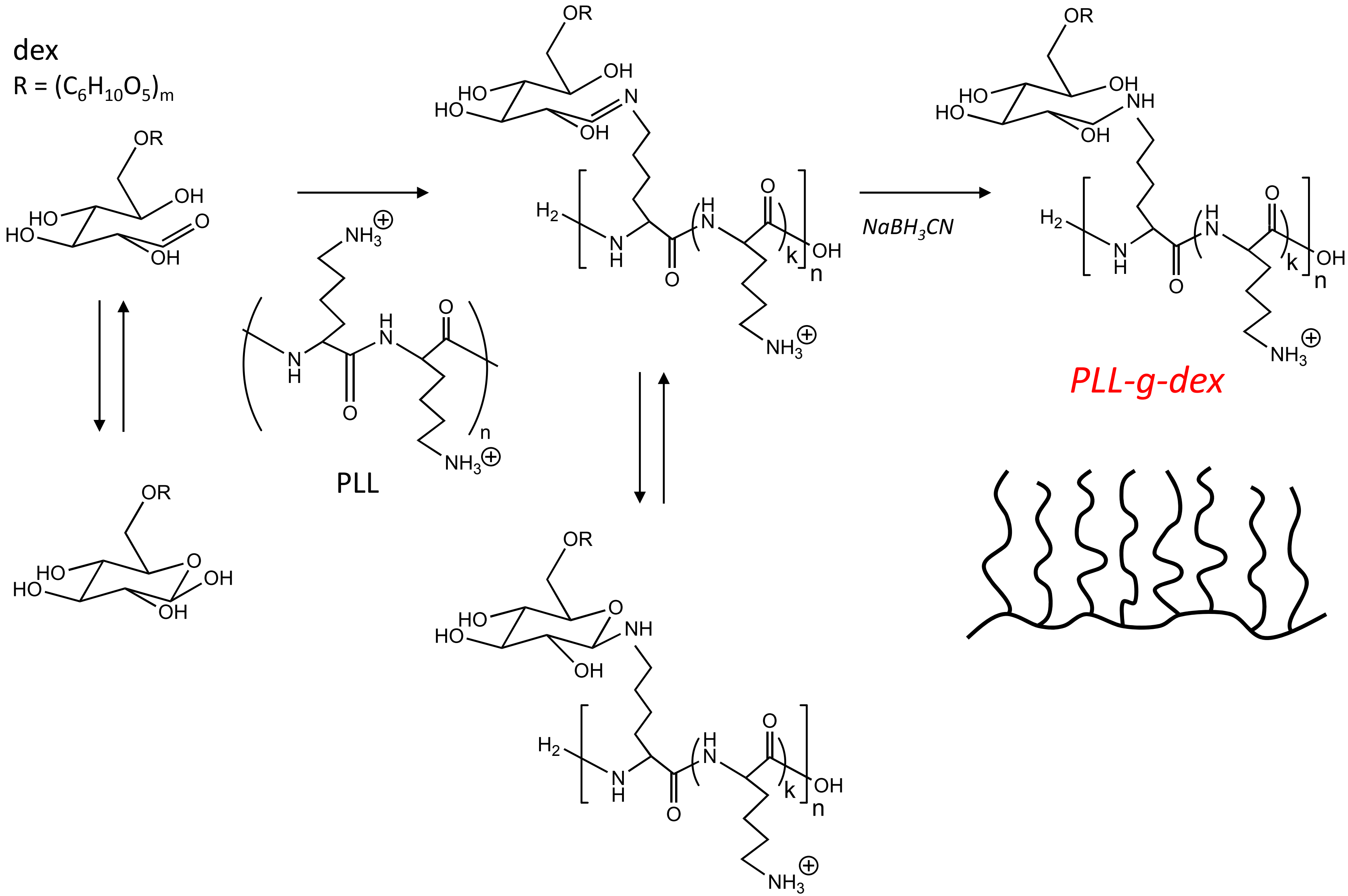
Schematic representation of the Lubricin (PRG 4)





Zappone B et al, Langmuir **2008**, 24, 1495.

Synthesis of Poly(L-lysine)-*g*-Dextran



Synthesis of Poly(L-lysine)-*g*-Dextran

From poly(L-lysine)-g-poly(ethylene glycol), PLL-g-PEG...

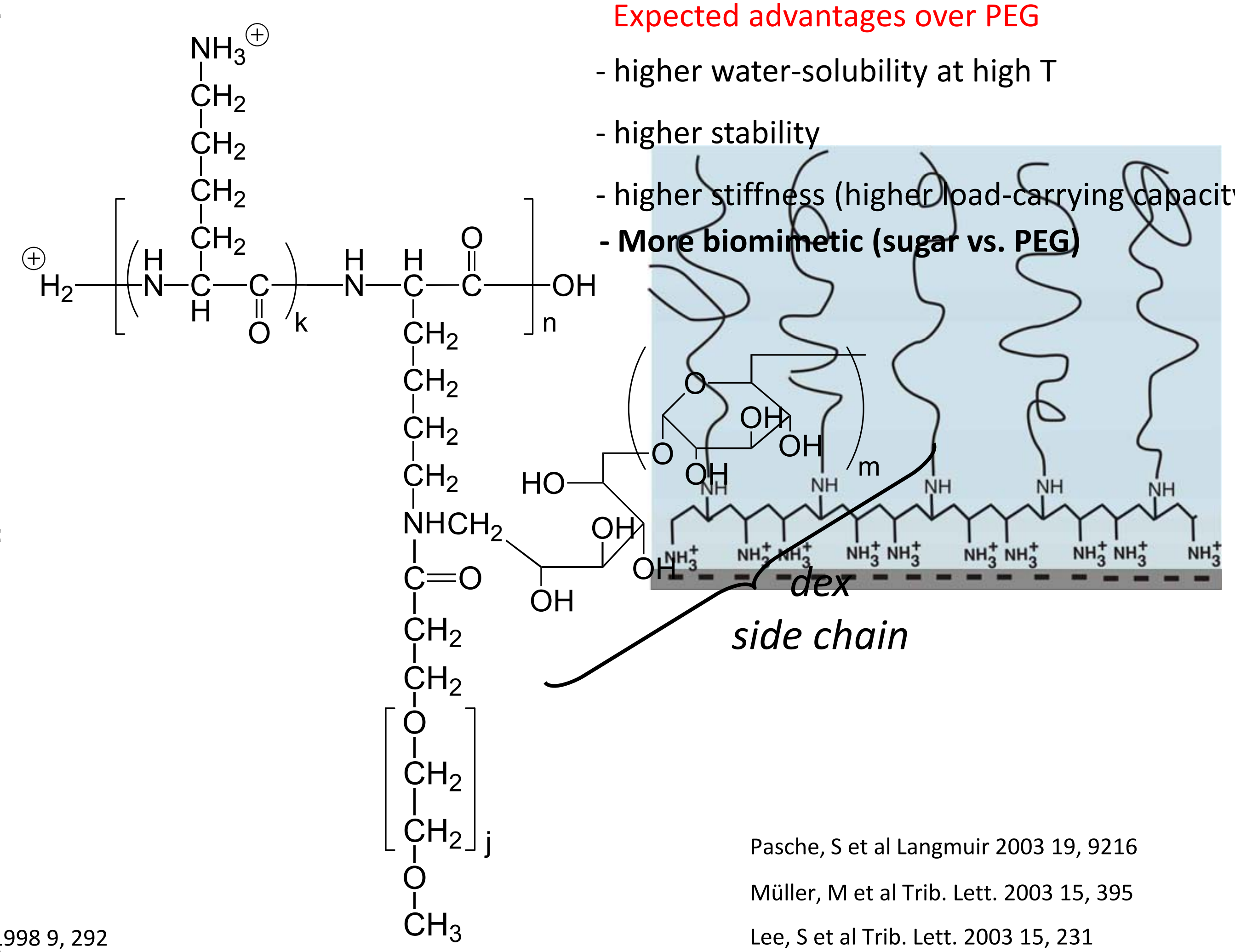
to poly(L-lysine)-g-dextran, PLL-g-dex

Expected advantages over PEG

- higher water-solubility at high T
- higher stability
- higher stiffness (higher load-carrying capacity)
- **More biomimetic (sugar vs. PEG)**

PLL backbone

PEG side chain



Perrino, C et al Langmuir 2008 24, 8850

Perrino, C et al, Trib. Lett. 2009 33, 83

Maruyama, A et al, Bioconjugate Chem. 1998 9, 292

Pasche, S et al Langmuir 2003 19, 9216

Müller, M et al Trib. Lett. 2003 15, 395

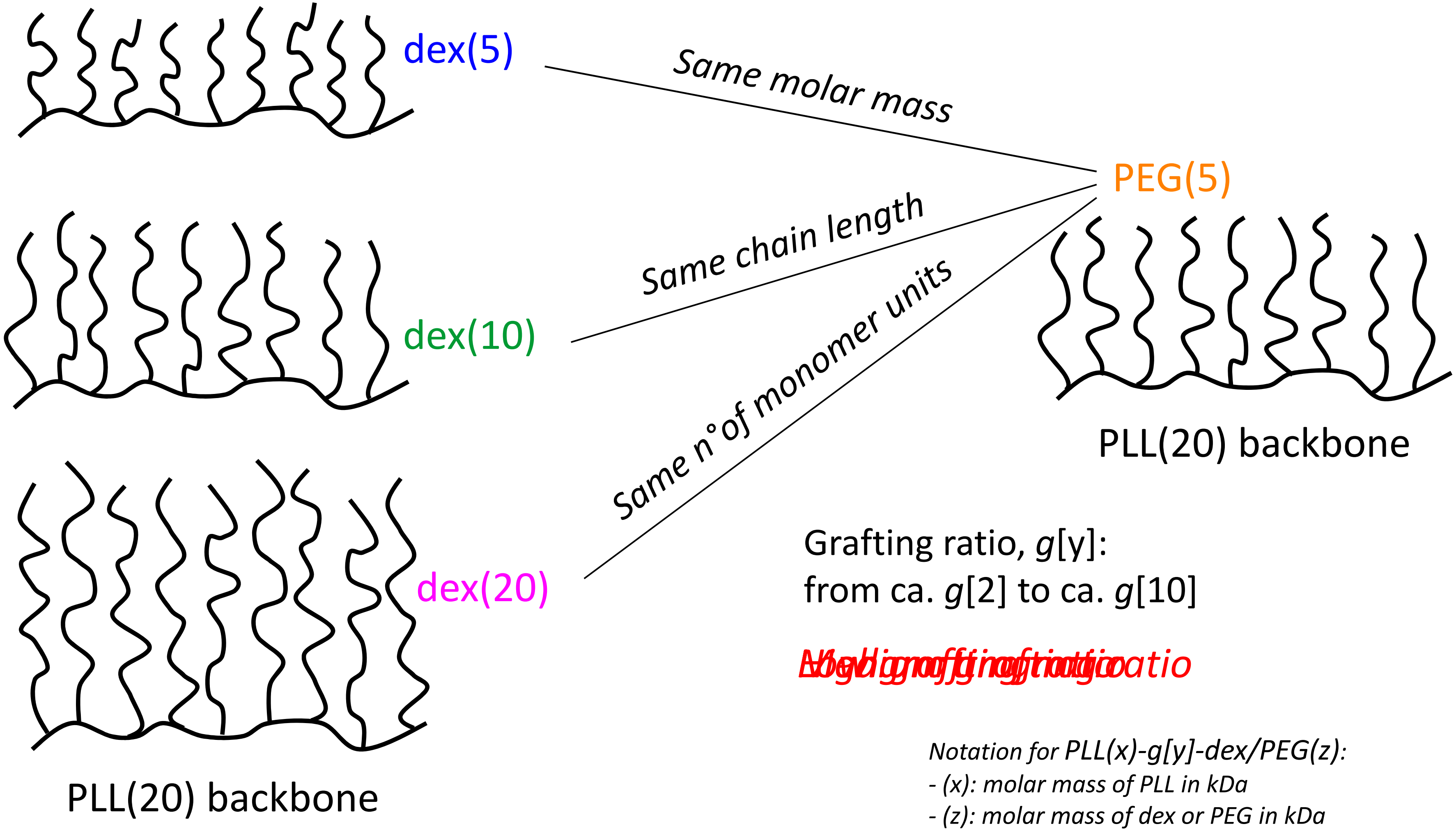
Lee, S et al Trib. Lett. 2003 15, 231

PLL-*g*-Dex: Architectural parameters

PLL(20)-*g*[y]-dex(z)

PLL(20)-*g*[y]-PEG(5)

provided by SuSoS AG

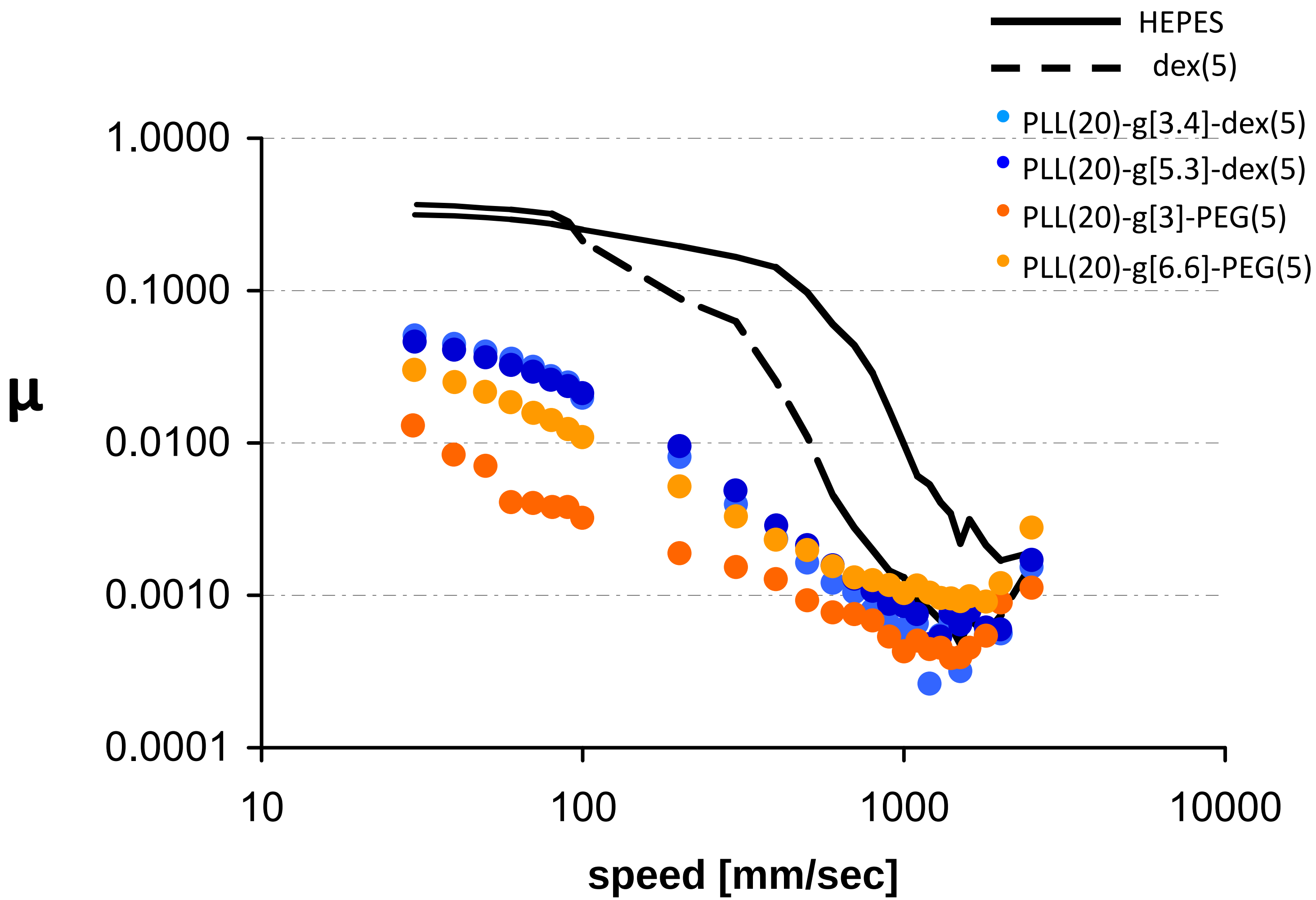


Grafting ratio, *g*[y]:
from ca. *g*[2] to ca. *g*[10]

[illegible] grafting ratio

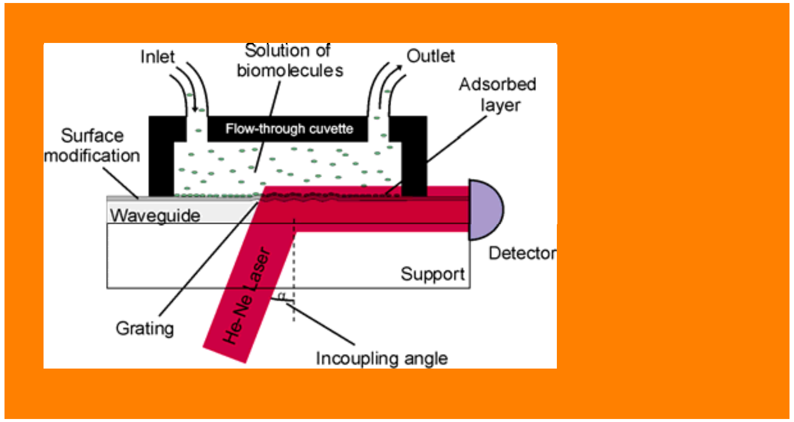
Notation for PLL(x)-g[y]-dex/PEG(z):
- (x): molar mass of PLL in kDa
- (z): molar mass of dex or PEG in kDa
- g[y]: number of lysine monomers/side chain

PLL-*g*-Dex: Lubricating properties – beating PLL-*g*-PEG?

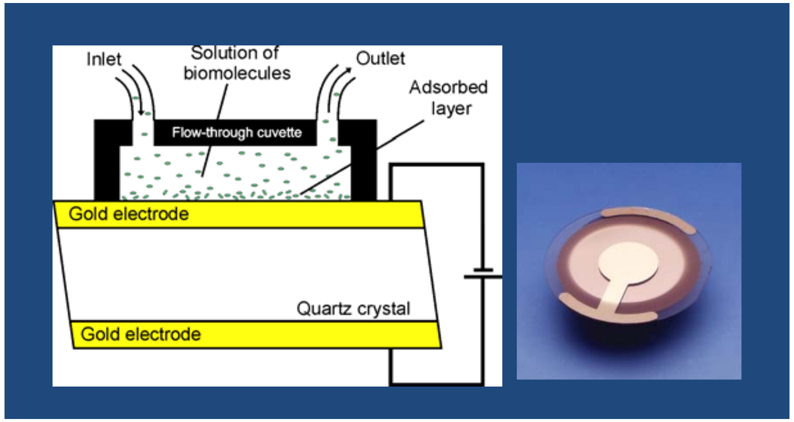


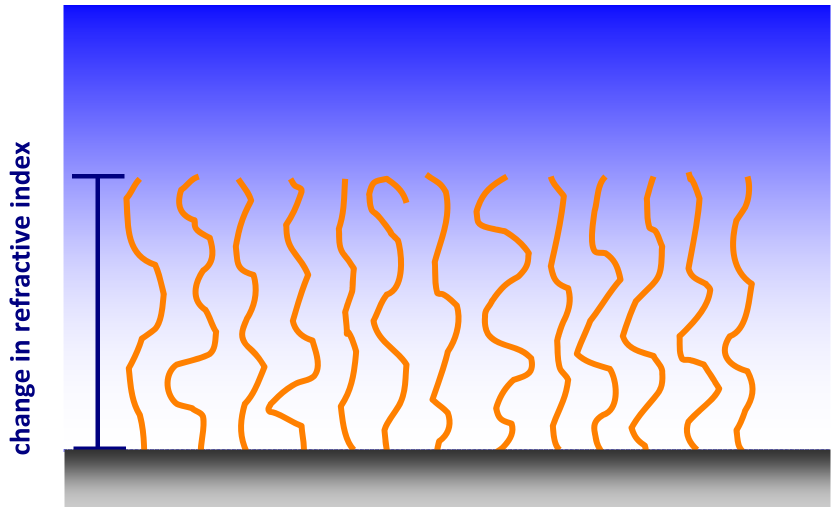
Hydration capacity of surface-bound dextran and PEG

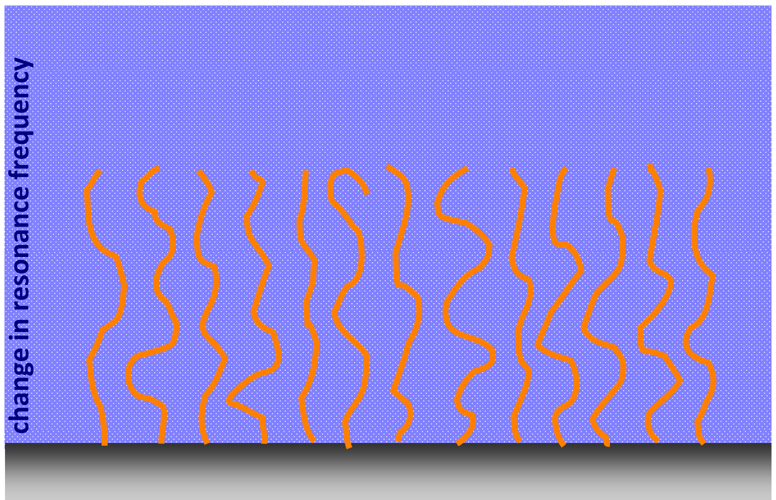
Optical Waveguide Lightmode Spectroscopy (OWLS)



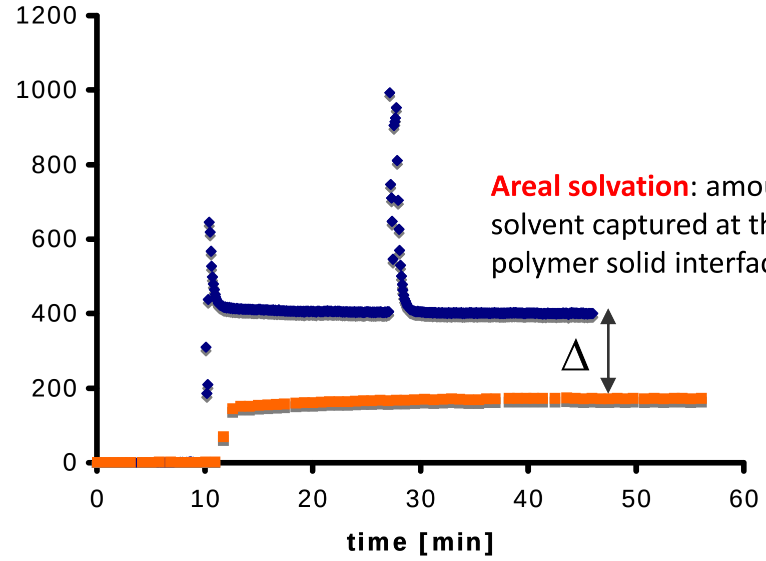
Quartz Crystal Microbalance with Dissipation mode (QCM-D)





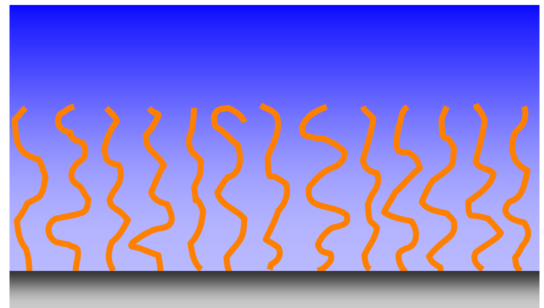


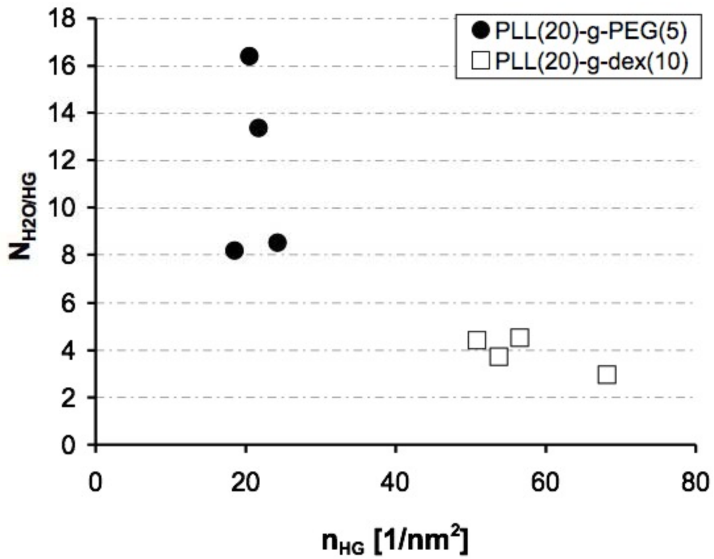
Hydration capacity of surface-bound dextran and PEG



Areal solvation: amount of solvent captured at the polymer solid interface

*m*ass (QCM-D) - *m*ass (OWLS)

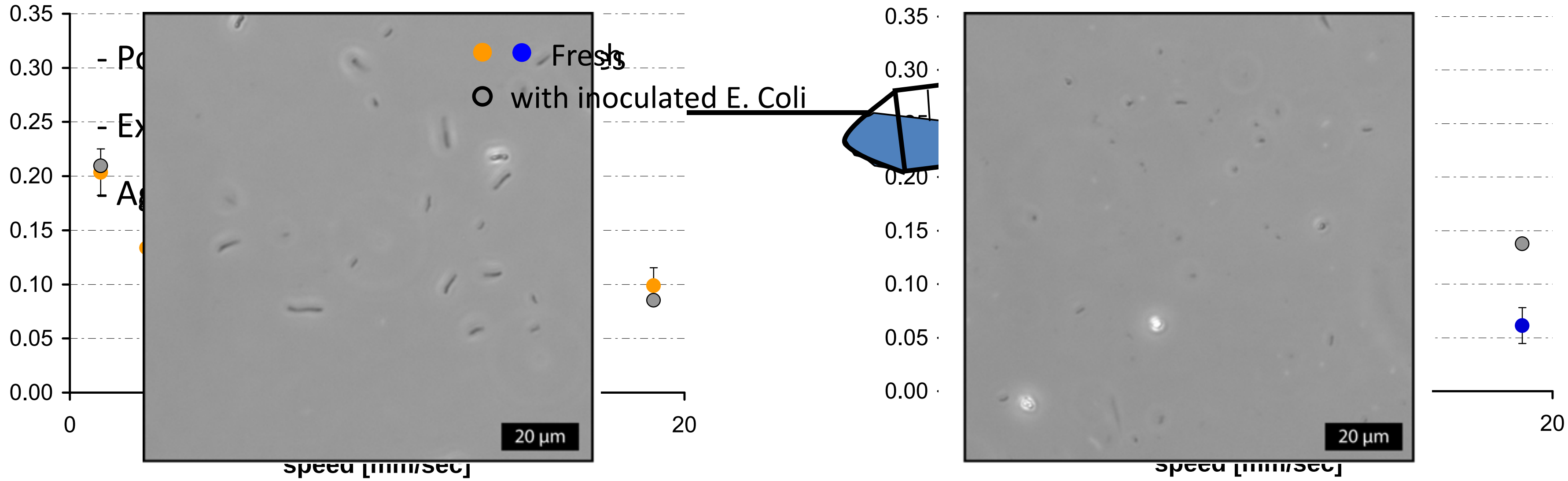


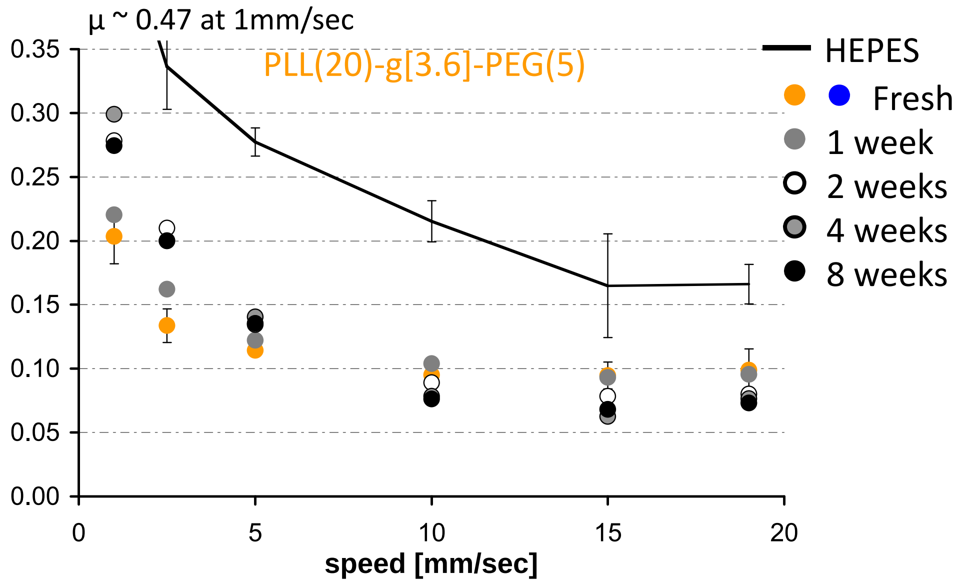


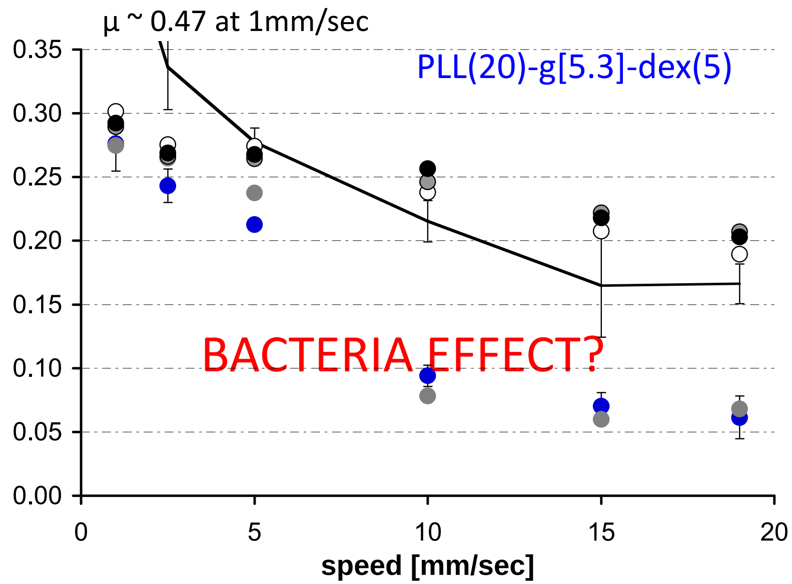
Basic hydration: 2-3 strongly bound water molecules per EG

Kjellander, R. et al J. Chem. Soc., Faraday Trans. 1981 1, 2053

Aging effect on the lubrication behavior

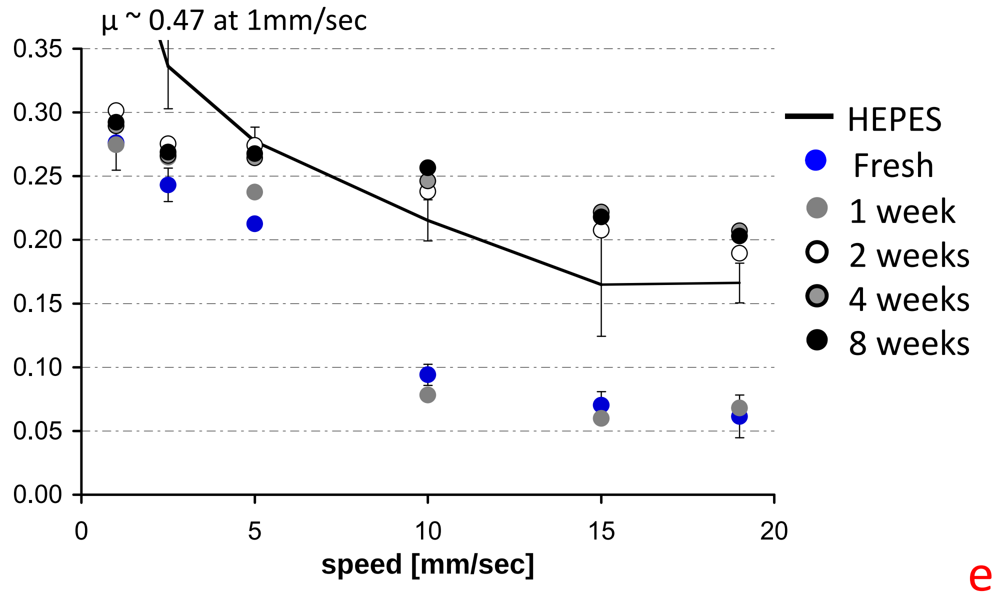




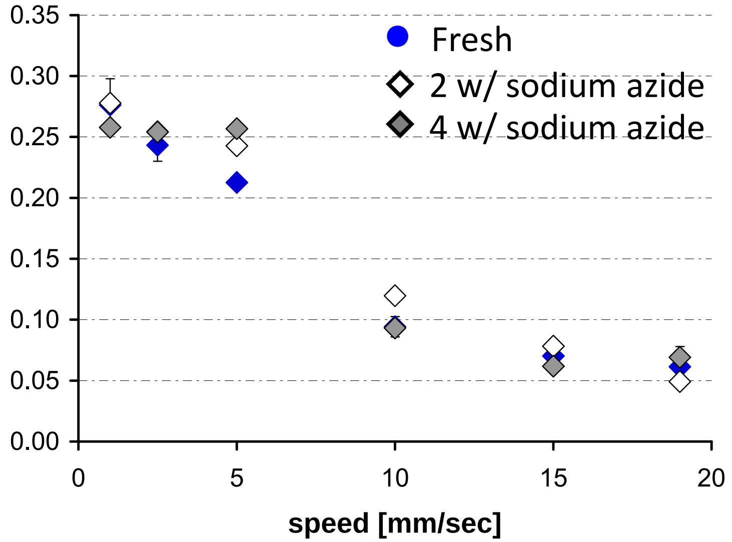


How to prevent bacteria-induced degradation?

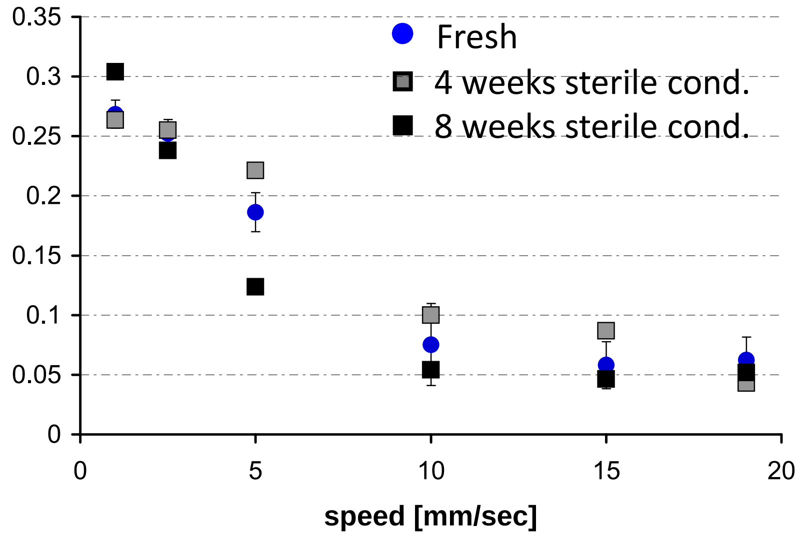
PLL(20)-g[5.3]-dex(5)



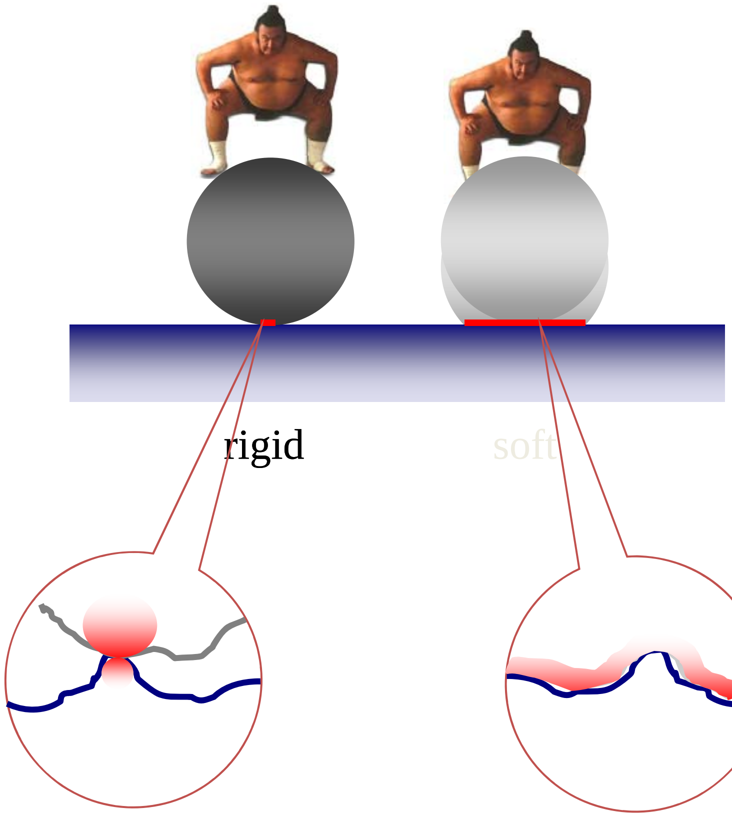
Use of a biocide



Sterile environment



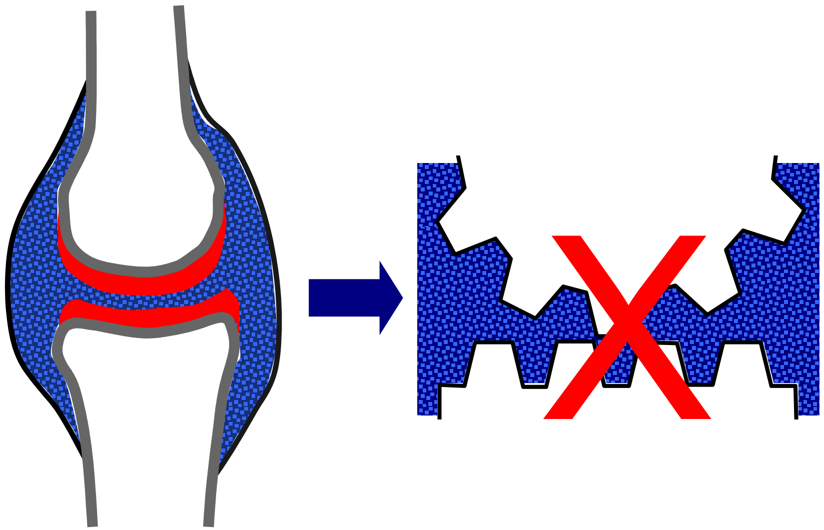
Nature's approach to use water as lubricant – recipe 2



low(er) contact pressure

little (reduced) necessity to increase the viscosity against external loads

feasible formation of lubricating film



Soft Elastohydrodynamic Lubrication (soft EHL)

Hamrock, Dowson, Esfahanian

Hamrock, B.J. and Dowson, D., Proc. 5th Leeds-Lyon symp. on Trib. 22-27 (1979)
Esfahanian, M. and Hamrock, B.J., Tribol. Trans. 34, 628-632 (1991)

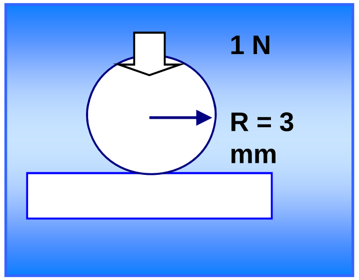
Hard EHL $\quad h_{min} = 1.79\, R^{0.47} \alpha^{0.49} \eta_0^{0.68} U^{0.68} E^{-0.12} W^{-0.07}$

Soft EHL $\quad h_{min} = 2.8\, R^{0.} \eta_0^{0.65} U^{0.65} E^{-0..44} W^{-0.21}$

α : pressure coefficient of viscosity

Soft contact: PDMS vs. PDMS

Rigid contact: steel vs. steel

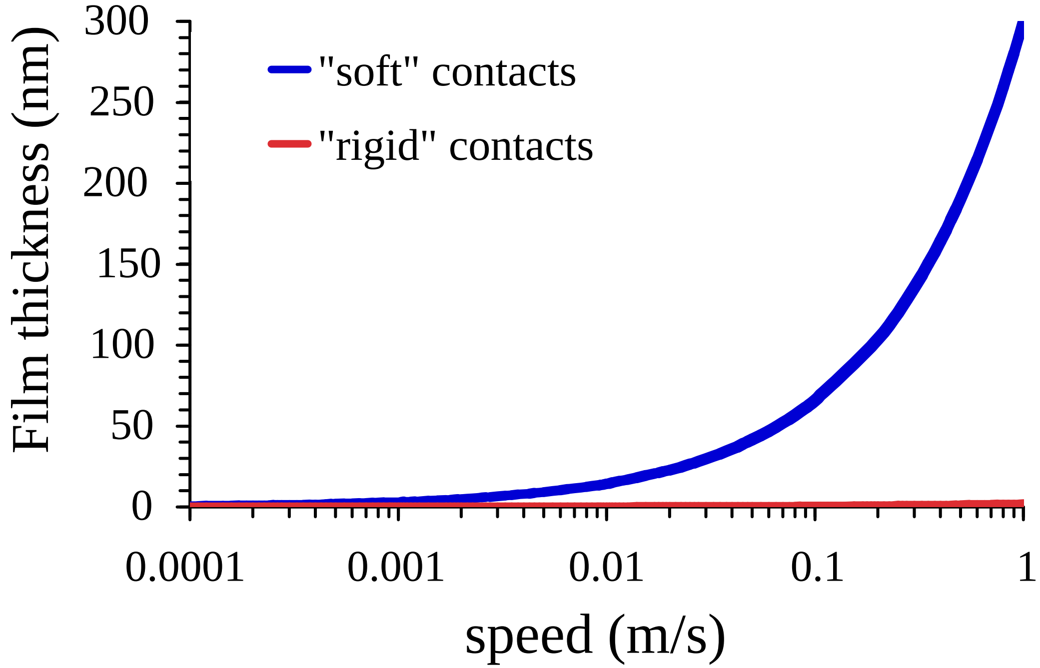


E (PDMS) = 2 MPa

ν (PDMS) = 0.5

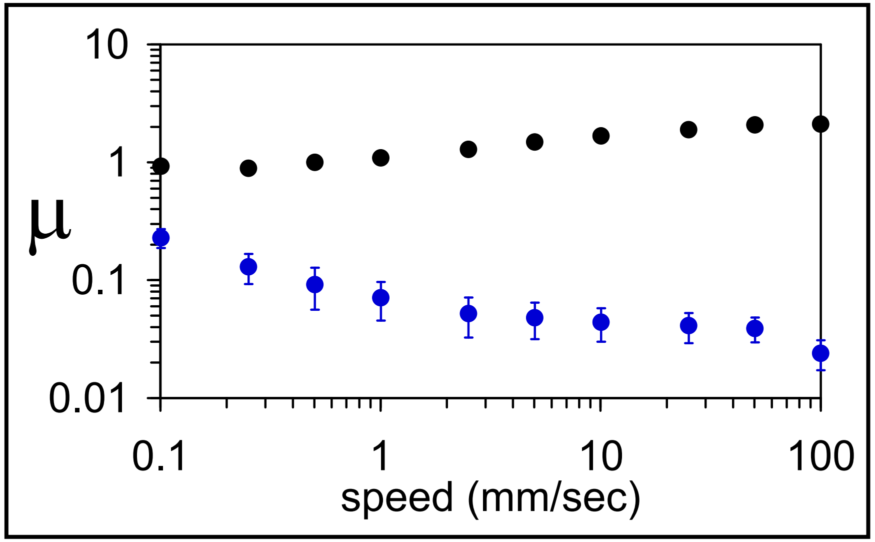
E (steel) = 200 GPa

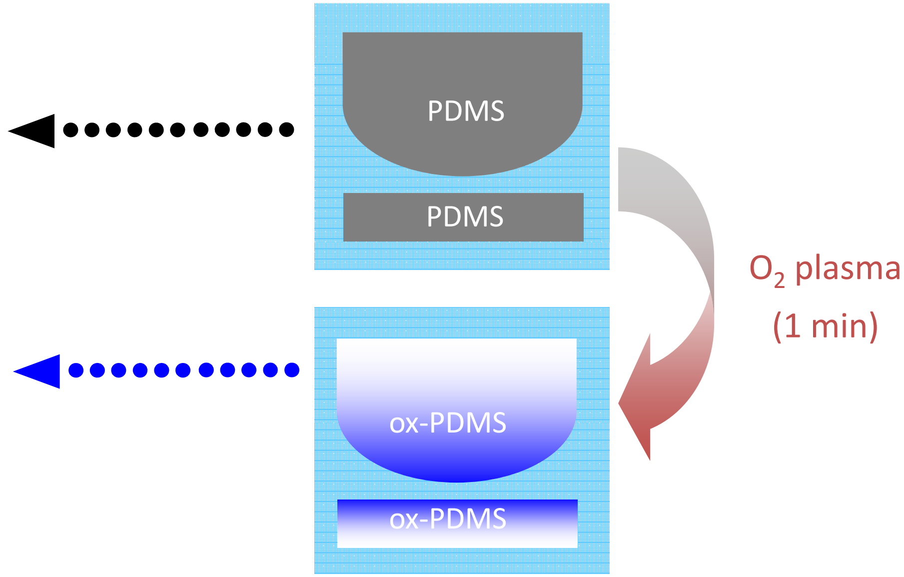
ν (steel) = 0.3



In reality ....

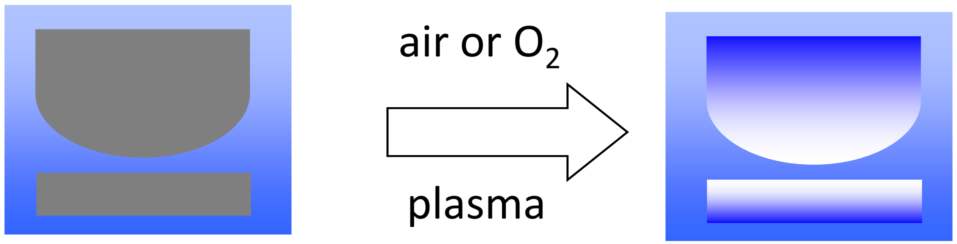
Role of surface hydrophilicity





load = 1 N, Hertzian contact pressure ca. 0.5 MPa

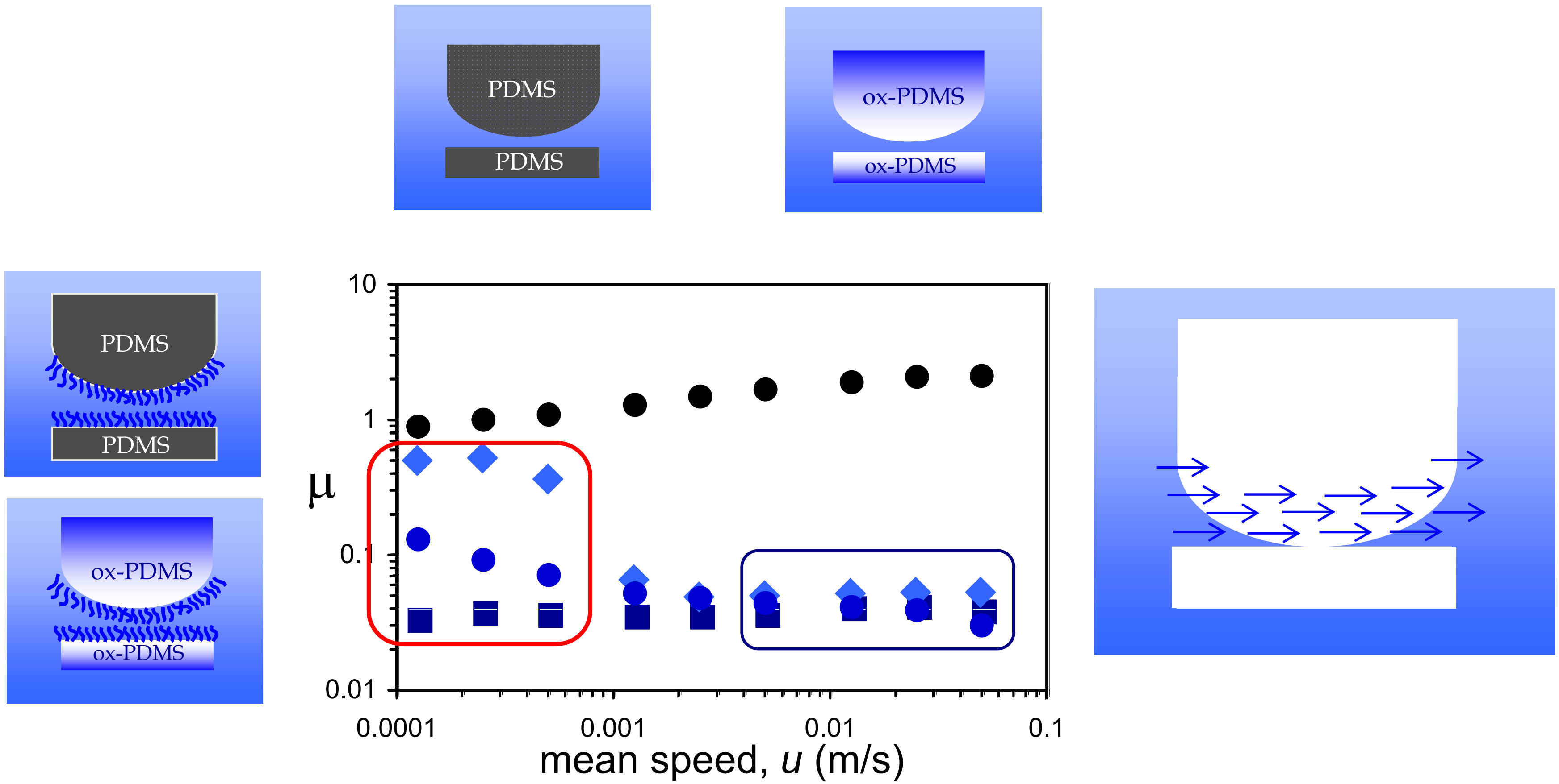
*S. Lee et al., **Tribol. Int**. 2005, 38, 922*



No significant change in bulk mechanical properties

Hydrophilization of surface (-OH and/or -COOH groups)

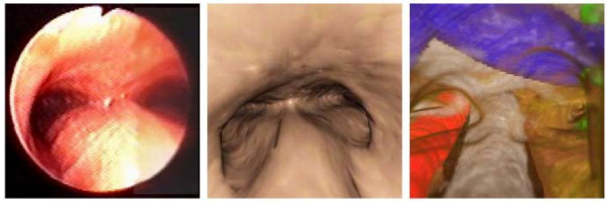
Influence of surface chemical modification

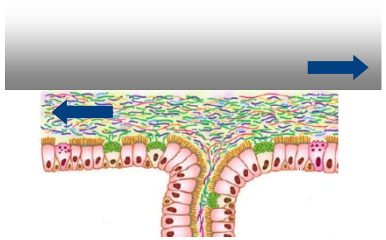


S. Lee et al., **Tribol. Int**. 2005, 38, 922

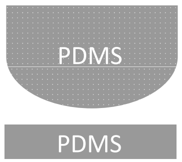
Soft contacts: model systems for tissue-contacting devices

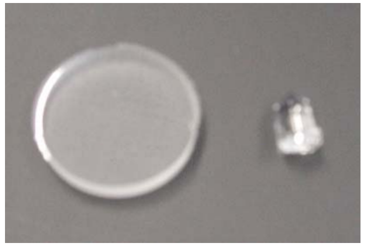
catheter, endoscope, cytoscope etc.





Poly(dimethylsiloxane) (PDMS)





Given conditions

- requires biocompatibility (anti-biofouling) *and* lubricity

PEG a good candidate!

- materials: mostly hydrophobic surfaces

- only surface coatings, but no (liquid) lubricant allowed

- contact pressure is very low

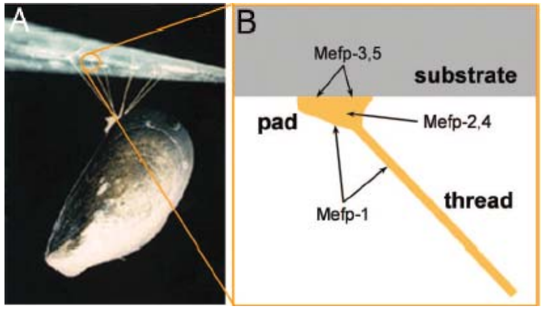
- no long or cyclic lubrication service

(1) Low-contact pressure

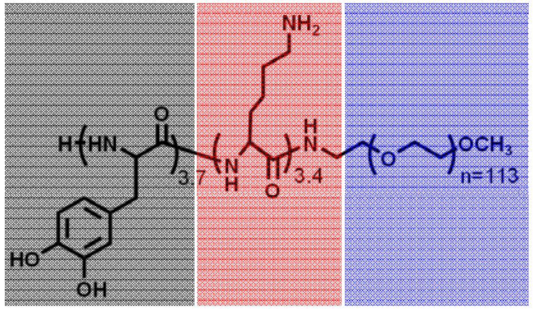
(2) Biomedical applications of silicone rubbers

(3) Comparison with other PEG-based copolymers

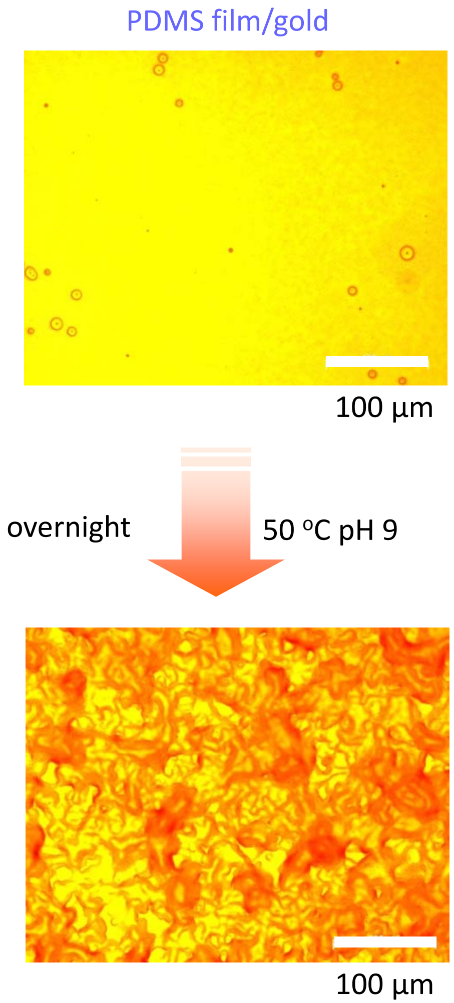
DOPA-Lysine-PEG



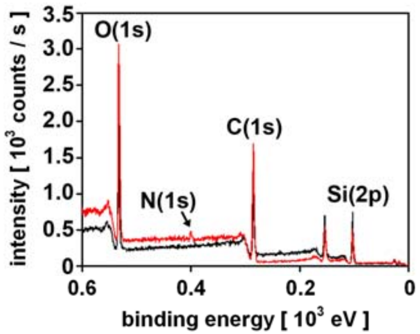
H. Lee et al, **PNAS**, 2006, 103, 12999

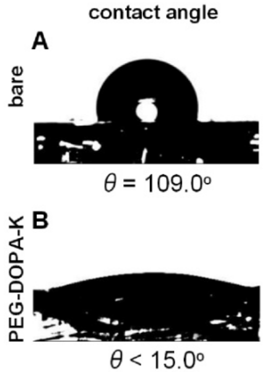


DOPA Lysine PEG (5 kDa)

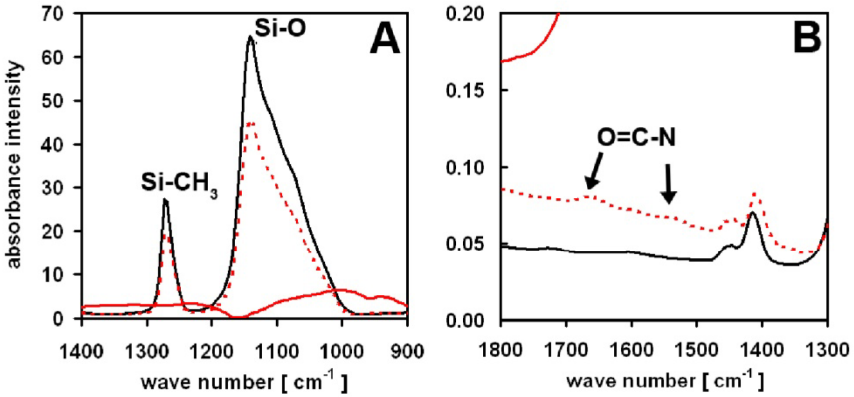


XPS

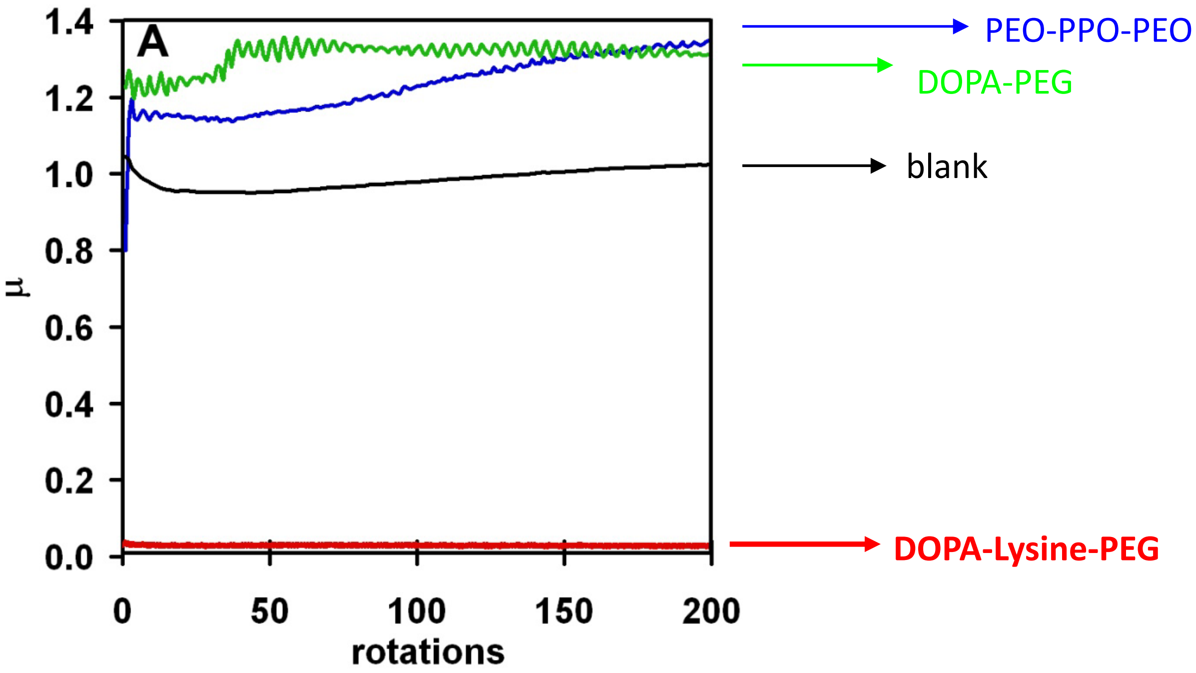


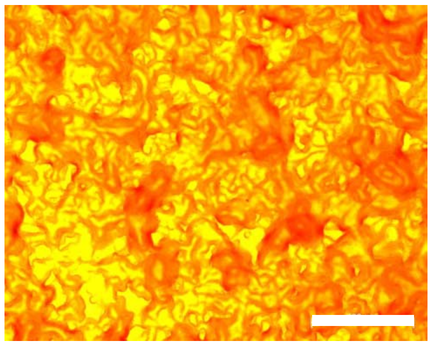


PM-IRRAS

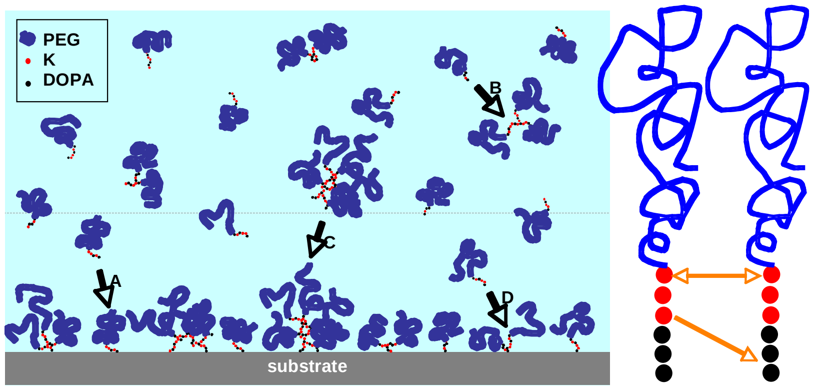


DOPA-Lysine-PEG





100 μm

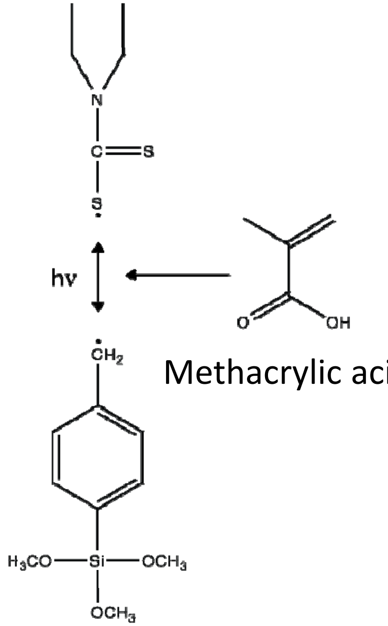


K. Chawala et al., **J. Biomed. Mater. Res. A** 2009, 90A(3). 742-749

Soft contacts: compatibility with "Grafting-from" approach

- Expected advantages
  - Substantially improved film thickness (µm range)
  - Charged polymer chains
  - Diverse chemical functionality

- Photoiniferter technique
  - UV-irradiation controlled radical polymerization
  - Reversible termination
  - Room temperature
  - Aqueous media
  - No sacrificial initiator

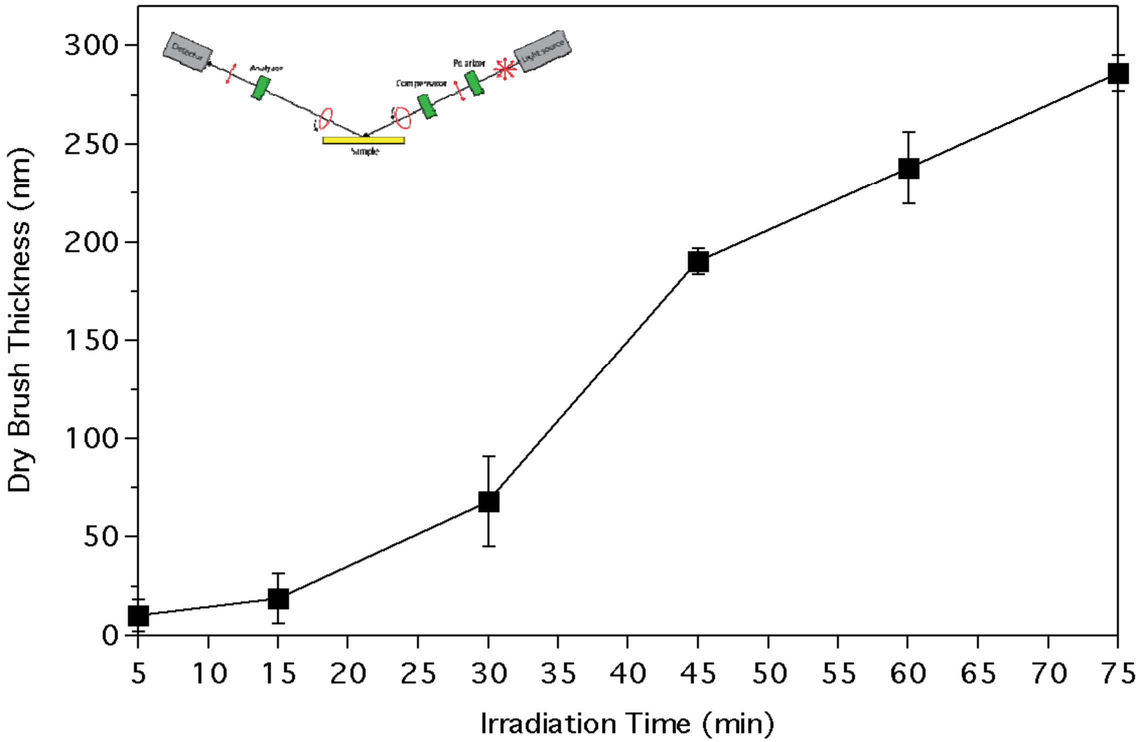


Methacrylic acid

N,N-(Diethylamino)dithiocarbamoyl-benzyl(trimethoxy)silane

UV-LED-Initiated grafting from Si/SiO_2 surfaces

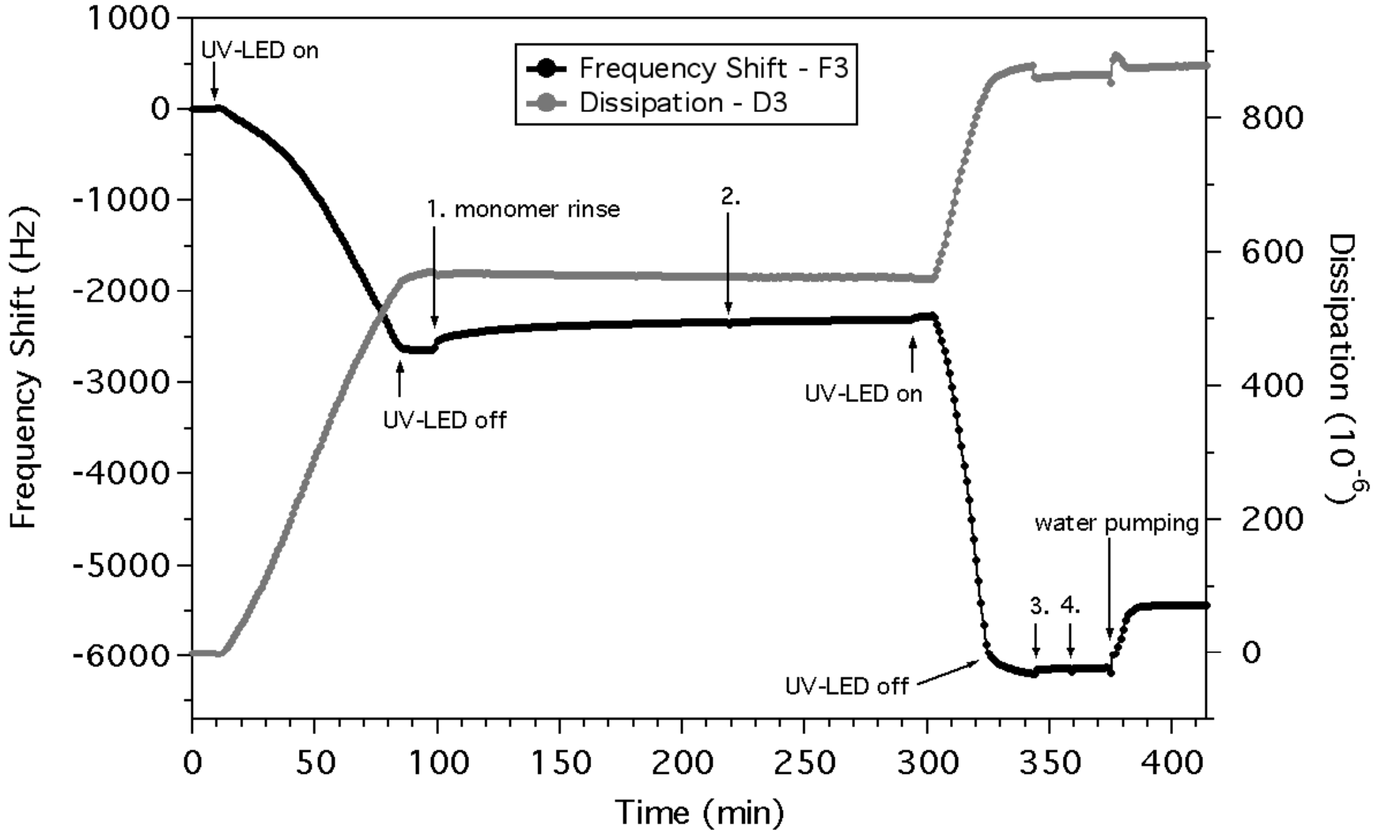
Controlled growth of high-density poly(methacrylic acid) (PMAA) brushes with high molecular weights

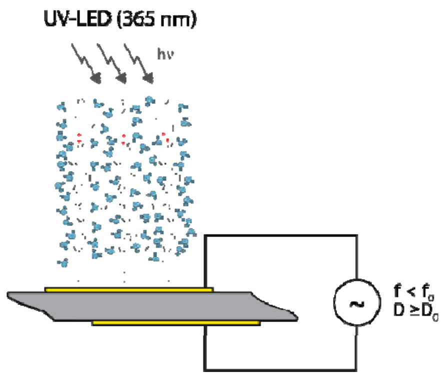


$$M_{w_{PMAA}} = L_{PMAA}{}^{2} d_{PMAA} \rho_{dry_{PMAA}} N_A$$

t (min)	d_{PMAA} (nm)	M_{wPMAA} (g / mol)
5	10	4'233
15	20	8'467
30	70	29'633
45	190	80'433
60	240	101'600
75	290	122'767

QCM-D - *In situ* PMAA Polymerization

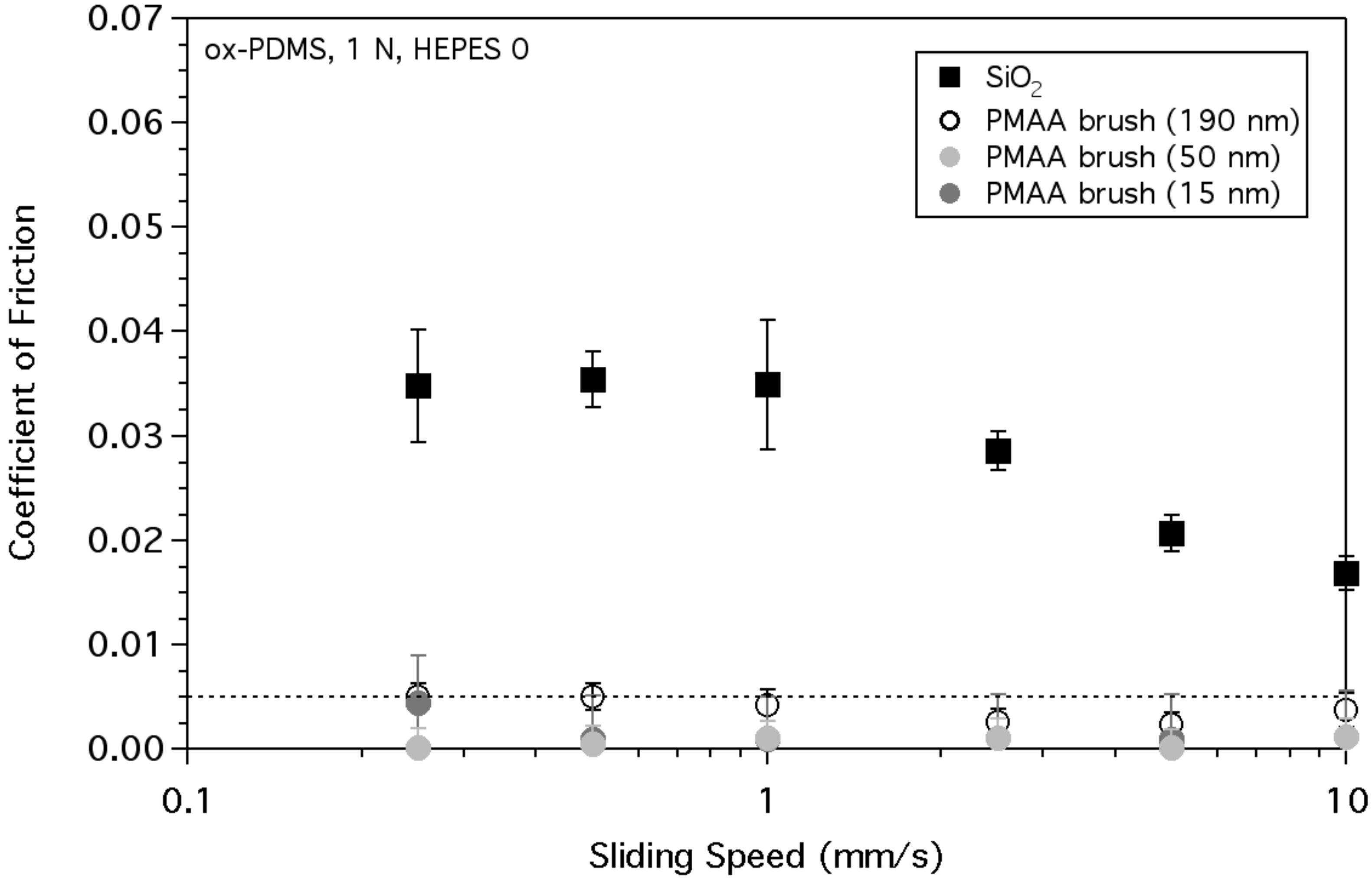


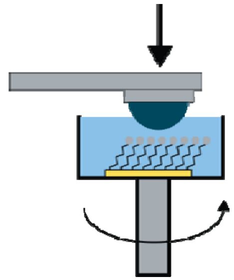


Rapid growth of PMAA brush with little bulk polymerization

Reactive chain ends preserved → second polymerization step

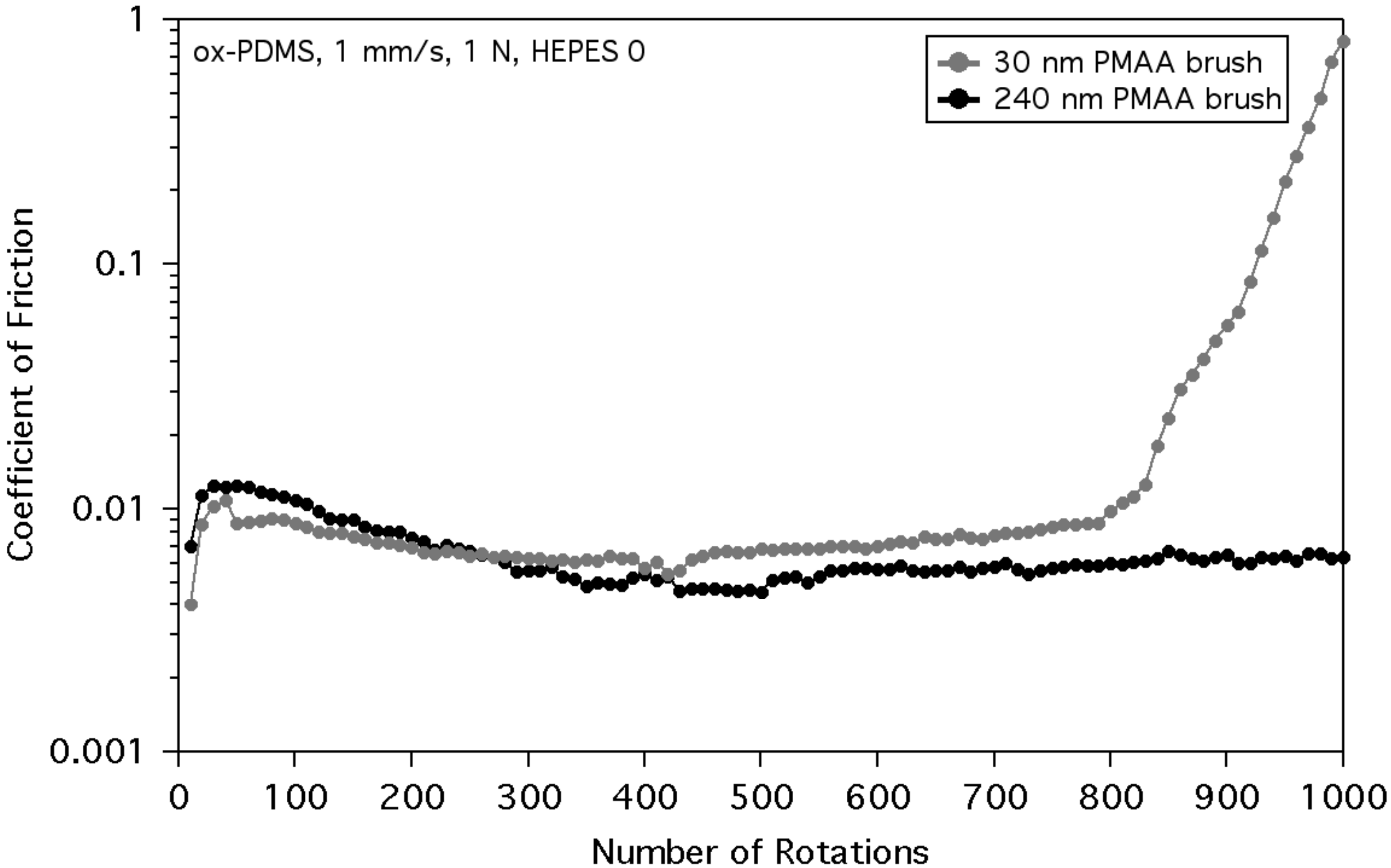
Aqueous Lubrication of PMAA Brushes

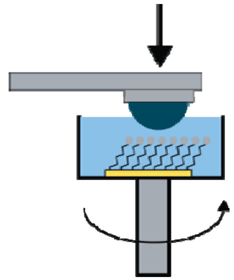




Frictional response from all PMAA brushes below detection limit

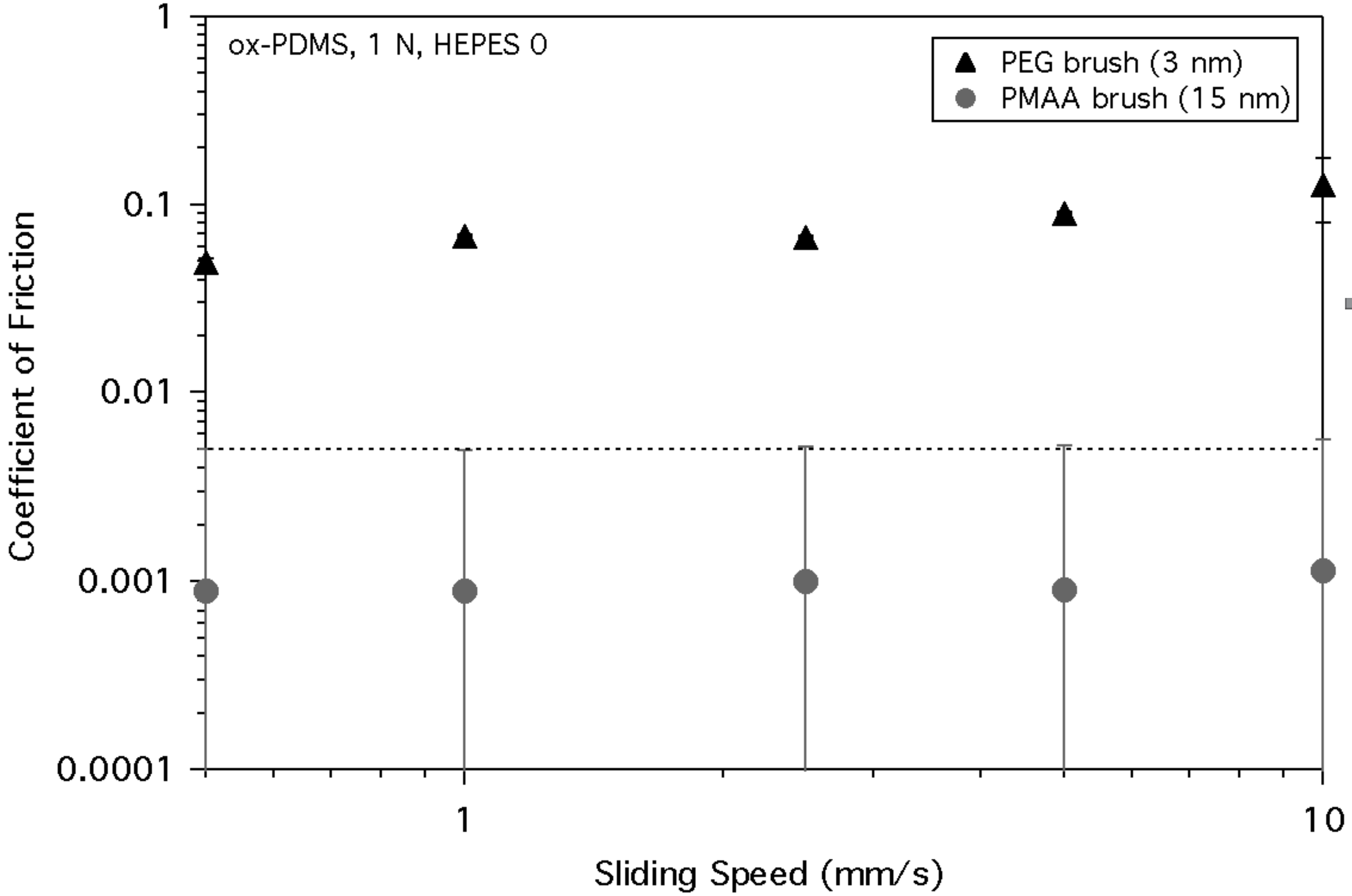
Long-term Aqueous Lubrication Performance

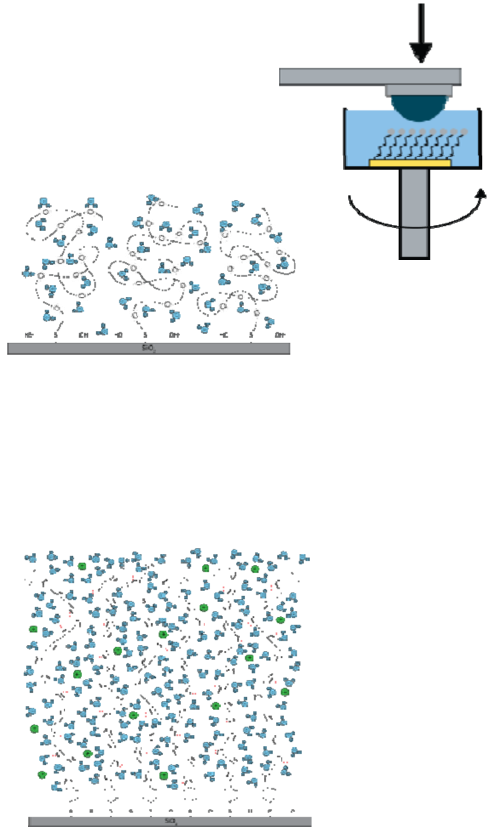




Good long-term stability of long PMAA brush
Short PMAA brush fails after prolonged sliding

Si-PEG vs. PMAA





High-density, polyelectrolyte brush exhibits superior aqueous lubrication properties compared to Si-PEG(5000)

Summary

Aqueous lubricating properties are generally improved by addition of brush-forming polymers into water

PEG (and PEG-based copolymers) has been most widely investigated for its unique solubility and hydration capabilities in water

Polyelectrolytes and/or carbohydrates are most promising to reveal more favorable aqueous lubricating properties than PEG

Attachment approach of brush-forming polymer chains can be flexibly selected depending on specific tribological application conditions

Thank you

for your attention